

VOLUME 29

JUNE 1951

NUMBER 6

Canadian Journal of Chemistry

***Editor:* J. W. T. SPINKS**

***Published by* THE NATIONAL RESEARCH COUNCIL
OTTAWA CANADA**

CANADIAN JOURNAL OF CHEMISTRY

This was formerly *Section B, Canadian Journal of Research*. The change to the new name took place January 1, 1951. The CANADIAN JOURNAL OF CHEMISTRY is published twelve times annually.

The CANADIAN JOURNAL OF CHEMISTRY is published by the National Research Council of Canada under the authority of the Chairman of the Committee of the Privy Council on Scientific and Industrial Research. Matters of general policy are the responsibility of a joint Editorial Board consisting of members of the National Research Council of Canada and the Royal Society of Canada.

The CANADIAN JOURNAL OF CHEMISTRY and the CANADIAN JOURNAL OF TECHNOLOGY have been chosen by the Chemical Institute of Canada as its medium of publication for scientific papers.

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SYNTHÈSE DES ACIDES AMINÉS À PARTIR DE LA RHODANINE¹

par ROGER GAUDRY et ROBERT A. McIVOR

Summary

The Gränacher method has been investigated to discover its applicability to the synthesis of a variety of natural amino acids. The procedure has been simplified for phenylalanine and tyrosine, and extended to valine and isoleucine. An unusual product of the oximation of α -thioketo- β -(*p*-methoxyphenyl)propionic acid is described.

Introduction

La rhodanine a eu plusieurs applications dans les synthèses organiques (20, 23, 24, 25). En 1922, Gränacher *et al.* (21, 22) ont publié une nouvelle synthèse des acides aminés à partir de la rhodanine. Bien qu'ils aient obtenu des rendements élevés, la méthode n'a eu qu'un usage restreint jusqu'à aujourd'hui. Puisque la rhodanine est actuellement un produit commercial, nous avons pensé que cette méthode pourrait être utilisée pour une synthèse pratique de plusieurs acides aminés.

La méthode de Gränacher consiste à condenser une aldéhyde ou une cétone avec la rhodanine (I), et à scinder le produit de condensation (II) avec une solution alcaline, pour obtenir ainsi l'acide α -thionique (V). Ces acides peuvent être transformés en oximes (VI) ou en phénylhydrazones (VII), qu'on peut facilement réduire par plusieurs méthodes pour obtenir les acides aminés correspondants (VIII).

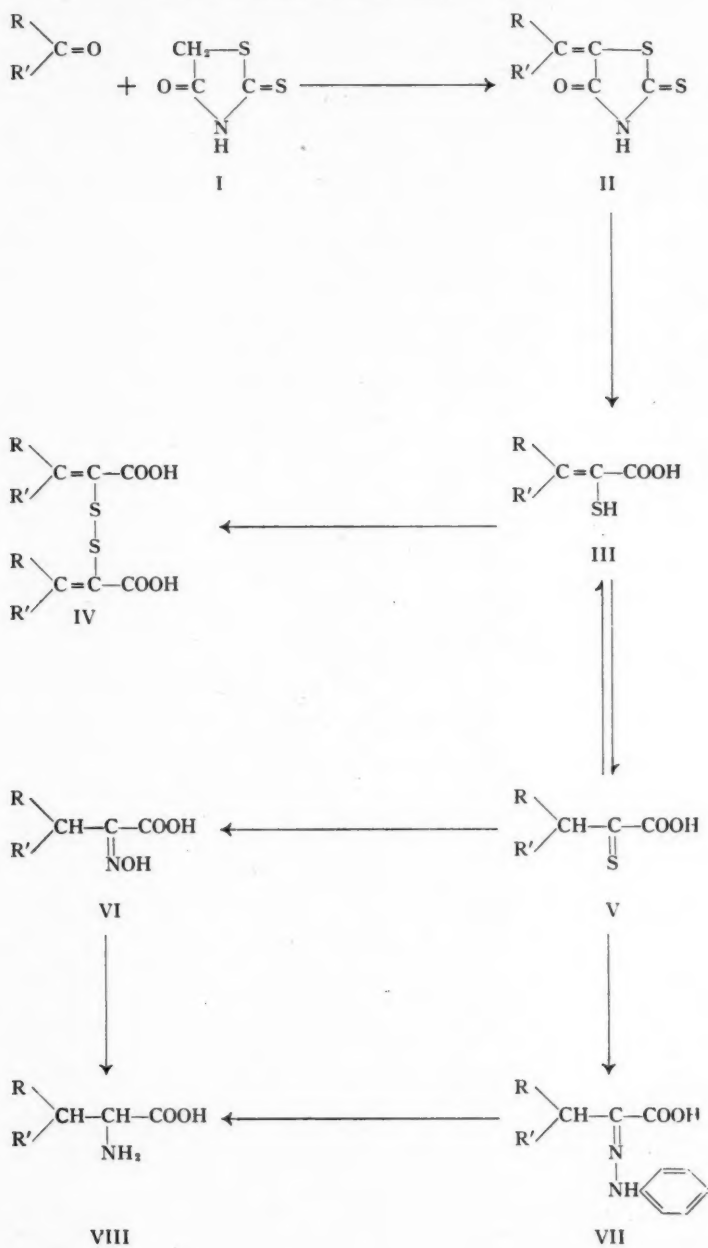
Gränacher a utilisé cette méthode pour préparer la phénylalanine, la furylalanine, l'O-méthyltyrosine, et la pipéronylalanine avec des rendements totaux de 50-58%. De plus, plusieurs acides aminés qui contenaient les radicaux thényles et pyrroles (7, 28) furent ainsi préparés. Cependant, on n'avait pas préparé auparavant d'acides aminés aliphatiques par cette méthode.

On sait depuis longtemps que la rhodanine peut être condensée quantitativement avec les aldéhydes aliphatiques, aromatiques et hétérocycliques, ainsi qu'avec les α -dicétones (21, 22, 23, 31). Andreasch et ses collaborateurs ont préparé des centaines de produits venant de condensations de rhodanine et d'aldéhydes*. Quand nous avons commencé ces recherches, on n'avait pas encore rapporté de condensation entre la rhodanine et des cétones simples, mais plus récemment, deux articles ont paru sur ce sujet (5, 6).

¹ Manuscrit original reçu le 15 décembre 1950, corrigé, le 9 février 1951.

Contribution du Département de Biochimie de la Faculté de Médecine, Université Laval, Québec, P.Q.

* Pour une liste complète de ses publications, voir la référence No. 21.



Les condensations peuvent être effectuées soit en milieu acide (27), soit en milieu basique (5, 19), mais la condensation en milieu basique a l'avantage de donner un produit moins coloré et plus cristallin, et donne un meilleur rendement avec les cétones aliphatiques.

Il n'est pas possible d'isoler à l'état pur les acides α -thioniques résultant de la scission des produits de condensation de la rhodanine avec les cétones aliphatiques de faibles poids moléculaires. On n'obtient que des huiles qu'il est impossible de distiller. Cependant, en cherchant à préparer l'acide α -thionique à partir de l'isopropylidène rhodanine, nous avons obtenu de petites quantités (5 à 10%), d'un solide qui possède, croyons nous, la formule IV (R et $R' = CH_3$). En effet, il a déjà été démontré que la rhodanine donne par réaction avec les alcalis un produit analogue (18). De plus, son point de fusion est beaucoup plus élevé que celui qu'on pourrait s'attendre à trouver pour le monomère. Le composé ne donne d'ailleurs pas de réaction au chlorure ferrique, comme c'est le cas pour les α -thioacides. Si l'on introduit un agent oxydant tel que le chlorure ferrique dans le mélange réactionnel, ou même simplement en y faisant barbotter de l'air, on peut porter le rendement du produit solide à 55%. Il faut ajouter que ce composé vient d'être rapporté dans la littérature (6). On n'en donne pas la structure, mais on y mentionne cependant le fait qu'il se comporte comme un dimère de l'acide α -thionique. Gränacher lui-même a été incapable d'isoler et de caractériser les acides α -thioniques aliphatiques et personne n'en a jamais préparé les oximes ou les phénylhydrazones. Tous nos essais de précipitation des acides α -thioniques aliphatiques sous forme de sels ont échoué de même que nos tentatives pour en préparer les oximes.

Les oximes des acides α -thioniques aromatiques ont généralement été préparées en solution alcoolique absolue. Elles peuvent cependant l'être plus facilement à partir des acides α -thioniques en solution alcaline aqueuse, en solution alcoolique diluée, ou en solution acétique diluée. La façon la plus convenable de les préparer consiste à ajouter directement du sulfate d'hydroxylamine au mélange qui résulte de la scission du produit de condensation. On peut préparer les phénylhydrazones d'une façon analogue. Ces préparations peuvent être effectuées en grandes quantités, alors qu'il vaut mieux isoler les acides α -thioniques en petites quantités (27).

Bien que nous n'ayons pas réussi à synthétiser les oximes des acides aliphatiques, nous en avons cependant préparé les phénylhydrazones avec de faibles rendements (25 à 30%) par addition de chlorhydrate de phénylhydrazine au mélange obtenu par scission des produits de condensation.* Il est probable qu'on pourrait en augmenter les rendements en ajoutant la phénylhydrazine au moment même où la réaction de scission commence, parce qu'il

*Au cours d'une de ces expériences, nous avons isolé comme sous-produit un solide, fondant à 110°C., insoluble dans les solutions alcalines, et qui semble être, à l'analyse, la phénylhydrazone de la méthyléthylcétone. Ce composé n'est pas rapporté dans la littérature comme étant un solide, peut-être parce qu'on l'obtient généralement sous forme d'un mélange des deux isomères possibles. La phénylhydrazone de l'acétone, qui ne peut exister que sous une seule forme, est aussi un solide.

semble que des quantités appréciables d'acides α -thioniques sont détruites au cours de la réaction.

Gränacher a employé l'amalgame de sodium pour réduire les oximes. Bien que les rendements soient bons, cette méthode n'est pas facilement applicable sur une grande échelle.

Nous avons trouvé que les oximes peuvent être réduites par l'hydrogène à basse pression en présence de nickel Raney W-6 ou W-7 (1) ou encore avec le nickel Raney *in situ*. Dans ce cas, les rendements furent de 30 à 50%. Les oximes peuvent aussi être réduites par la méthode de Feofilaktov (8), ce qui donne des rendements d'environ 10% pour la réduction. La réduction électrolytique est celle qui donne les rendements les plus élevés, soit 75 à 80%.

Des essais de réduction de l'acide α -oximino- β -phénylpropionique avec la poudre de zinc et l'acide acétique de même qu'avec l'étain et l'acide chlorhydrique n'ont pas réussi, bien qu'il soit possible de réduire ainsi l'acide α -oximino- β -(*p*-méthoxyphényl)propionique.

La préparation des phénylhydrazones à partir des acides α -thioniques n'a pas été décrite jusqu'à présent, mais elle est assez facile. Les phénylhydrazones peuvent être facilement réduites chimiquement. Feofilaktov se sert de zinc et d'une solution alcoolique d'acide chlorhydrique à 0°C. pour réduire ces phénylhydrazones. Il a prétendu ainsi obtenir des rendements quantitatifs dans ses publications antérieures (8,9,10,11,12) mais plus récemment (13,14) il donne des rendements de 50 à 60% pour des composés analogues. Nous avons aussi obtenu de bons rendements bruts avec sa méthode, mais le produit n'était pas pur, dû probablement à la formation des indoles ou pseudoindoles correspondants. Après purification les rendements furent de 50 à 60%. Sa méthode est aussi passablement incommode pour les préparations sur une grande échelle. La méthode qui utilise la poudre de zinc et l'acide acétique concentré (mais pas glacial), est plus élégante, mais elle aussi ne donne que des rendements de 50 à 60% pour les phénylhydrazones aromatiques et de 20% pour la phénylhydrazone de l'acide diméthylpyruvique. Il ne semble pas possible de réduire électrolytiquement les phénylhydrazones.

Les points de décomposition de l'acide α -oximino- β -phénylpropionique donnés dans la littérature varient entre 155°C. et 173° à 174°C. (4). Le produit obtenu ordinairement se décompose avec dégagement abondant de gaz à 155°C. (non corrigé); mais dans d'autres préparations nous avons obtenu des produits qui se décomposent à 172°C. et 206°C. Un réarrangement de Beckmann avec l'acide sulfurique sur les isomères qui se décomposent à 172°C. et à 206°C. a donné la phénylacétamide dans les deux cas. Nous croyons maintenant que ces oximes sont capables d'énolisation et qu'ainsi les isomères seraient interconvertibles en solution. De plus, tous les deux pourraient donner la phénylacétamide par déshydratation et décarboxylation, suivie d'hydrolyse. L'isomère qui fond à 155°C. se forme en présence d'un très grand excès d'hydroxylamine, et les autres quand il n'y a qu'un excès de trois

molécules-grammes d'hydroxylamine. Par traitement des isomères ayant les points de fusions les plus élevés par l'hydroxylamine en solution alcaline, on obtient l'isomère qui fond à 155°C.

Gränacher déclare (21) avoir synthétisé l'acide phénylpyruvique par l'hydrolyse de cette oxime avec la formaldéhyde et l'acide chlorhydrique tandis que Hall, Hynes et Lapworth (26) ont obtenu un rendement de 50% de α -hydroxy- β -phényl- γ -crotonolactone avec les mêmes réactifs en proportion différente. Nous avons répété les expériences des deux, et nous avons trouvé que toutes les deux sont correctes, mais qu'il est difficile de purifier l'acide phénylpyruvique obtenu par la méthode de Gränacher, parce qu'il est contaminé par la lactone. Cette lactone ne se condense pas avec la rhodanine.

Le point de fusion de l'acide α -oximino- β -(*p*-méthoxyphényl)propionique donné dans la littérature est 159°C. (22), tandis que notre produit fond à 199°C. (déc.). Cet isomère donne en solution alcaline avec l'hydroxylamine un autre isomère qui fond à 144°-145°C. (déc.).

Le traitement de l'acide α -thio- β -(*p*-méthoxyphényl)propionique par l'hydroxylamine donne en plus de 50% de l'oxime, environ 20% d'un composé inconnu qui se décompose avec dégagement abondant de gaz à 147.5°-148°C. Ce composé est soluble dans les bases, mais insoluble dans les acides dilués. Par pyrolyse, il se décompose en plusieurs gaz, dont l'ammoniaque et le bioxyde de carbone. Il réduit la liqueur de Fehling à froid, et réagit immédiatement avec le permanganate et l'eau de brome. Il réduit l'acide périodique en l'iode. Une partie demeure inchangée par réaction avec le pentachlorure de phosphore et l'isocyanate de phényle. Les valeurs trouvées pour le poids moléculaire sont les suivantes:

Par l'analyse Kjeldahl (2 atomes d'azote)	245
Par la méthode de Rast (32)	241
Par titrage du groupement carboxyle	238

Par réduction avec l'étain et l'acide chlorhydrique on obtient un dichlorhydrate d'un acide aminé. Il est en effet possible de titrer trois-groupements acidiqes différents, dont les équivalents chimiques sont: 285, 145 et 90.5. Par dissolution de ce chlorhydrate dans l'éthanol absolu, suivie de l'addition de pyridine, on obtient un précipité d'un monochlorhydrate instable qu'on peut transformer en picrate.

L'oxydation du produit inconnu original par le permanganate de potassium en solution alcaline à 0°C. a donné l'acide α -oximino- β -(*p*-méthoxyphényl)propionique avec un point de fusion de 144.5°C. Cette oxime fut réduite par l'étain et l'acide chlorhydrique en O-méthyltyrosine, identifiée sous forme de dérivé phényluréidé, p.f. 165° à 166.5°C. (dec.). Le point de fusion ne fut pas abaissé par mélange avec un échantillon authentique.

Nous croyons que ce composé peut être l'acide α,α -dihydroxylamino- β -(*p*-méthoxyphényl)propionique.

Nous n'avons pas réussi à préparer d'acides aminés en traitant directement les produits de condensation des aldéhydes aromatiques avec la rhodanine par l'ammoniaque sous pression, ni même en chauffant les acides α -thioniques avec l'ammoniaque selon la méthode de Galat (16).

La phénylalanine et l'O-méthyltyrosine peuvent ainsi être facilement et rapidement synthétisées en grandes quantités à partir de la rhodanine, par condensation en milieu ammoniacal avec la benzaldéhyde ou l'anisaldéhyde, scission avec la soude caustique, suivie de l'addition de l'hydroxylamine sans isoler l'acide α -thionique, et réduction électrolytique de l'oxime ainsi obtenue. On transforme ensuite l'O-méthyltyrosine en tyrosine par chauffage à reflux avec un mélange d'acide chlorhydrique concentré et d'acide acétique glacial. Quant à la valine et à l'isoleucine, nous avons démontré que leur synthèse est possible par la méthode à la rhodanine, mais elle ne présente qu'un intérêt théorique à cause des faibles rendements des produits intermédiaires.

Partie Expérimentale

Benzalrhodanine (II: R = C₆H₅; R' = H)

A un mélange de rhodanine (120 g., 0.904 mole) et de chlorure d'ammonium (80 g. dissous dans 160 ml. d'eau chaude), on ajoute une suspension de benzaldéhyde (96 g., 0.904 mole) dans l'ammoniaque à 28% (80 ml.). Après deux ou trois minutes d'agitation, le mélange se solidifie. On le laisse refroidir et on le verse dans trois litres d'eau froide. Par filtration, on obtient 196 g. (98%) d'un précipité jaune orangé, assez pur pour les réactions subséquentes. Par recristallisation de l'alcool aqueux, on obtient des aiguilles jaunes. P.f. 199° à 200°C.* Litt.: 200°C. (30).

On peut préparer la *p*-hydroxybenzalrhodanine et l'anisalrhodanine d'une façon analogue avec des rendements pareils. Mais l'anisalrhodanine forme souvent des masses dures qui renferment de l'anisaldéhyde n'ayant pas réagi.

La *p*-hydroxybenzalrhodanine est une poudre jaune (recristallisée de l'éthanol). P.f. 275° à 285°C. (déc.). Litt.: 260°C. (3), 274°C. (2).

L'anisalrhodanine forme des aiguilles rouges brunâtres (recristallisée de l'éthanol). P.f. 249° à 254°C. (déc.). Litt.: 230° à 242°C. (3), 230° à 232°C. (22).

Les produits de condensation entre la rhodanine et les aldéhydes n'ont pas de points de fusion nets, et le point de fusion peut dépendre de la vitesse avec laquelle on chauffe le capillaire.

Isopropylidène Rhodanine (II: R = R' = CH₃)

A un mélange de rhodanine (30 g., 0.226 mole) et de chlorure d'ammonium (20 g. dissous dans 40 ml. d'eau chaude), on ajoute une suspension d'acétone (40 ml., 0.454 mole) dans l'ammoniaque à 28% (20 ml.). Le produit de condensation commence parfois à précipiter tout de suite. On chauffe à reflux

* Les points de fusion ne sont pas corrigés.

pendant une heure, et on verse le mélange dans l'eau froide (1500 ml.). Les petits granules jaunes pâles qui se forment sont assez purs pour les réactions subséquentes. Rendement: 33 g. (84%). P.f. 194° à 196°C. Litt.: 196° à 197°C. (5). Calculé pour $C_6H_7NOS_2$: N, 8.09%. Trouvé (Kjeldahl): N, 8.17%.

Quand on prépare ce produit par la méthode de Julian et Sturgis (27), le produit initial fond aux environs de 130°C., mais on peut le purifier par recristallisation de l'éthanol dilué ou de l'acide acétique dilué. Si on le cristallise du benzène ou du toluène, on concentre l'impureté de rhodanine au dépens du produit de condensation.

On peut préparer l' α -méthylpropylidène rhodanine d'une façon semblable. Rendement: 70%. Elle cristallise (de l'éthanol aqueux ou de l'acide acétique aqueux) en granules jaunes. P.f. 122° à 123°C. Litt.: 119° à 120°C. (5). Calculé pour $C_7H_9NOS_2$: N, 7.49%. Trouvé: N, 7.41%.

Acide α -Thio- β -phénylpropionique (V: R = C_6H_5 ; R' = H)

On ajoute de la soude caustique à 15% (65 ml., 0.29 mole) à de la benzalrhodanine (12.5 g., 0.057 mole) dans une fiole conique et on chauffe 30 min. sur un bain-marie, suivi par deux minutes d'ébullition. On refroidit à 0°C., et on ajoute *rapidement* de l'acide chlorhydrique à 10% (100 ml.). Un précipité jaune se forme. Après une heure à 0°C., on filtre. Le produit est assez pur pour les réactions subséquentes. Rendement: 10.2 g., (100%). Il cristallise en aiguilles blanches (du toluène). P.f. 127° à 129°C. Litt.: 125° à 129°C. (21).

Les composés suivants furent préparés par une méthode semblable:

Acide α -thio- β -(*p*-hydroxyphényl)propionique. (Porté à ébullition pendant cinq minutes après le chauffage sur le bain-marie, ou encore chauffé à reflux pendant 30 min.). Rendement: 100% d'une poudre blanche ou jaune (recristallisé du toluène). P.f. 176° à 178.5°C. Litt.: 186°C. (2).

Acide α -thio- β -(*p*-méthoxyphényl)propionique. Rendement: 98% de feuilles jaunes (recristallisé du toluène). P.f. 178° à 180°C. Litt.: 178°C. (22).

N.B. Il est conseillé de ne pas scinder à la fois plus de 15 g. de produit de condensation si l'on veut isoler l'acide α -thionique.

Bisulfure de bis(α -Carboxy- β , β -diméthylvinyl-) (IV: R = R' = CH_3)

A. On ajoute de la soude caustique à 15% (36 g., 0.884 mole dissoute dans 250 ml. d'eau) à de l'isopropylidène rhodanine (40 g., 0.232 mole) dans une fiole conique et on chauffe pendant 30 min. sur un bain-marie, suivi par deux minutes d'ébullition. On refroidit à 0°C., on divise la solution en quatre parties, et on ajoute *rapidement* de l'acide chlorhydrique à 10% (80 ml. pour chaque partie). Des cristaux oranges se forment lentement. Rendement: 1.9 g., (6%). Granules oranges (recristallisés de l'eau). P.f. 172° à 175°C. Calculé pour $C_{10}H_{14}O_4S_2$: COOH, 34.4%; S, 24.4%. Trouvé: COOH, 34.6%, S, 24.2%.

B. On ajoute de l'isopropylidène rhodanine (17.2 g., 0.1 mole) à une solution de soude caustique à 15% (12 g., 0.3 mole, dissoute dans 56 ml. d'eau). On y fait barbotter de l'air pendant une heure. On acidifie rapidement avec de l'acide chlorhydrique à 1:1 (60 ml.) ce qui provoque la séparation d'une huile jaune. En faisant barbotter de l'air dans le liquide pendant une heure supplémentaire, l'huile cristallise en un solide jaune pâle. Rendement: 7.2 g., (55%). P.f. 175° à 184°C.

On peut aussi poursuivre l'oxydation en faisant la scission par la méthode usuelle, suivie par l'addition d'une solution concentrée de chlorure ferrique, goutte à goutte, jusqu'à ce que la coloration rouge du thiocyanate ferrique dure pendant plusieurs minutes. Rendement: 4.2 g. (31%).

Acide α -Oximino- β -phénylpropionique (VI: R = C₆H₅; R' = H)

On chauffe de la benzalrhodanine (95.3 g., 0.43 mole) avec de la soude caustique à 15% (72 g., 1.81 moles dissoute dans 411 ml. d'eau) pendant 30 min. sur un bain-marie, puis deux minutes à l'ébullition. On ajoute à cette solution chaude, de la soude caustique (36.0 g., 0.91 mole) et une solution aqueuse de sulfate d'hydroxylamine (223 g., 1.36 moles). Il y a un dégagement vigoureux d'acide sulfhydrique. On reporte la solution à l'ébullition pendant deux minutes, et on la laisse refroidir à la glacière. On filtre et on lave le précipité avec de l'acide chlorhydrique dilué. Par acidification du filtrat, on obtient parfois un précipité additionnel. Le premier précipité est généralement l'isomère qui fond à 155°C. (déc.). Le deuxième peut être n'importe quel isomère. Si l'on emploie la moitié de la quantité d'hydroxylamine mentionnée plus haut, l'oxime précipite seulement après acidification, la plupart du temps sous forme d'isomère fondant à 206°C. Après recristallisation de l'éthanol, on obtient 62.8 g. (81%) de cristaux blancs soit en aiguilles, soit en feuilles.

L'isomère qui fond à 155°C. est soluble dans l'eau, l'acétone et l'alcool chaud, peu soluble dans l'alcool froid, très peu soluble dans l'éther, le chloroforme, le dioxane et le benzène. L'isomère qui fond à 206°C. est moins soluble dans l'eau et plus soluble dans les solvants organiques. Calculé pour C₉H₉NO₃: N, 7.82%. Trouvé: N, 7.96% (155°C.); 7.23% (172°C.); 7.52% (206°C.).

On peut préparer l'acide α -oximino- β -(*p*-hydroxyphényl)propionique et l'acide α -oximino- β -(*p*-méthoxyphényl)propionique d'une façon analogue, bien qu'il soit conseillé de n'utiliser que la moitié du sulfate d'hydroxylamine.

Acide α -oximino- β -(*p*-hydroxyphényl)propionique. Rendement: 60% de granules bruns, assez purs pour les réactions subséquentes. P.f. 178.5° à 179°C.* (déc.). Calculé pour C₉H₉NO₄: N, 7.48%. Trouvé: N, 7.24%.

Avec l'anisalrhodanine et le sulfate d'hydroxylamine en milieu alcalin, on obtient un précipité d'un composé inconnu décrit plus haut avec un rendement de 20%. Il cristallise (de l'éthanol absolu) en aiguilles blanches. P.f. 147.5° à 148°C. (dec.). Après acidification, on obtient l'acide α -oximino- β -(*p*-méthoxy-

*Variable selon la vitesse de chauffage.

phényl)propionique avec un rendement de 50%, qui cristallise (de l'éthanol aqueux) en feuilles. P.f. 199°C. (déc.). Litt.: 159°C. (22). Calculé pour $C_{10}H_{11}NO_4$: N, 6.70%. Trouvé: N, 6.98%.

Phénylhydrazone de l'acide phénylpyruvique (VII: R = C_6H_5 ; R' = H)

On chauffe de la benzalrhodanine (30 g., 0.136 mole) avec de la soude caustique à 15% (18.2 g., 0.472 mole dissoute dans 104 ml. d'eau). Après que tout est passé en solution, on chauffe sur un bain-marie pendant 30 min. supplémentaires. On porte la solution à l'ébullition pendant deux minutes, et on y ajoute une solution aqueuse de chlorhydrate de phénylhydrazine (17 g., 0.136 mole). Après avoir laissé reposer toute la nuit, on centrifuge (si nécessaire) et on acidifie avec l'acide chlorhydrique en agitant rapidement avec un agitateur mécanique. Par filtration on obtient la phénylhydrazone sous forme d'une poudre jaune-orange. Rendement: 96% brut et 74% pur. Elle cristallise de l'éthanol aqueux en granules jaunes. P.f. 160° à 161°C. Litt.: 160° à 161°C. (33).

On prépare les phénylhydrazones suivantes d'une façon analogue:

Phénylhydrazone de l'acide *p*-hydroxyphénylpyruvique. Rendement: 96% (brut) et 75% (recristallisée de l'éthanol aqueux). Elle cristallise en granules bruns rougeâtres. P.f. 157°C. (déc.). Litt.: 159° à 161°C. (capillaire chauffé lentement) et 167° à 169°C. (déc.) (capillaire chauffé rapidement) (29).

Phénylhydrazone de l'acide *p*-méthoxyphénylpyruvique. Rendement: 100% (brut) et 80% (recristallisée de l'éthanol aqueux). Elle cristallise en aiguilles jaunes pâles. P.f. 141° à 142°C. On peut la séparer en deux isomères par cristallisation fractionnée de l'alcool absolu: un isomère incolore qui fond de 158° à 159°C. et un isomère jaune qui fond à 150°C. Litt.: 158° à 159°C. et 150°C. (13)*.

Phénylhydrazone de l'acide diméthylpyruvique. Rendement: 40% (brut) et 25% (recristallisée de l'éthanol aqueux). Elle cristallise en aiguilles jaunes ou de couleur chamois, très longues et minces. P.f. 143° à 144°C. (déc.). Litt.: 144°C. (12).

Phénylhydrazone de l'acide méthyléthylpyruvique. Rendement: 40-50% (brut) et 20% (recristallisée de l'éthanol aqueux). Elle cristallise en aiguilles jaunes pâles, très longues et soyeuses. P.f. 133.5°C. (déc.). Litt.: 132° à 133°C. (8).

dl-Phénylalanine (VIII: R = C_6H_5 ; R' = H)

A. On effectue l'hydrogénation pendant trois heures à la température de la chambre, de l'acide α -oximino- β -phénylpropionique (5 g., 0.028 mole) dissous dans 150 ml. d'eau en présence de nickel Raney W-6 (2 g.) comme catalyseur, à une pression de 2 à 3 atmosphères. On filtre le nickel Raney, on acidifie et on filtre à nouveau. On ajuste le pH à 5.9, on évapore à sec et on ajoute un peu d'eau pour solubiliser les sels inorganiques. Par filtration, on obtient de

* La cristallisation fractionnée a été faite par le docteur Karl F. Keirstead.

la phénylalanine. Rendement: 2.0 g., (43%). P.f. 239°C. à 244°C. (capillaire scellé). Litt.: 260° à 270°C. (21). L'hydrogénation ne réussit pas dans l'éthanol ou le dioxane. Calculé pour $C_9H_{11}NO_2$: N, 8.49%. Trouvé: N, 8.30%.

Le dérivé phényluridé cristallise en aiguilles blanches de l'éthanol aqueux. P.f. 174.5°C. (déc.). Litt.: 169° à 170°C. (17). Le point de fusion ne fut pas abaissé par le mélange avec un échantillon authentique. Calculé pour $C_{16}H_{16}N_2O_3$: N, 9.85%. Trouvé: N, 9.70%.

La réduction de l'acide α -oximino- β -(*p*-hydroxyphényl)propionique par cette méthode donne la *dl*-tyrosine avec un rendement de 20%. P.f. 291° à 293°C. Litt.: 290° à 295°C. (15). Calculé pour $C_9H_{11}NO_3$: N, 7.73%. Trouvé: N, 7.79%.

B. On dissout dans l'eau chaude de l'acide α -oximino- β -phénylpropionique (10 g., 0.056 mole) et on y ajoute de l'alliage de nickel Raney (25 g.). On porte la solution à reflux, et on ajoute de la soude caustique en pastilles une à une (ATTENTION) pendant trois à quatre heures, jusqu'à ce que l'aluminium soit entièrement dissous. On filtre, on ajuste le pH à 7-8 et on enlève l'hydroxide d'aluminium par filtration. On acidifie avec l'acide chlorhydrique concentré et on évapore à sec. On dissout le chlorhydrate de l'acide aminé dans l'éthanol absolu, on filtre les sels inorganiques et on ajoute de la pyridine en léger excès. Après avoir laissé 24-48 h. à la glacière, on filtre. Rendement: 4 g. (44%). P.f. 224° à 228°C. (capillaire scellé).

C. On place dans un ballon muni d'un agitateur mécanique et plongeant dans un bain de glace, une solution d'acide α -oximino- β -phénylpropionique (9 g., 0.05 mole) dans l'éthanol (100 ml.) et du zinc en poudre (9 g.).

On y ajoute, goutte à goutte, pendant trois à quatre heures, une solution d'acide chlorhydrique (15 g., 0.411 mole) dans l'éthanol. On filtre l'excès de zinc s'il en reste, on évapore à sec, on ajoute de l'eau, on évapore de nouveau à sec, on dissout le résidu dans l'eau, et on précipite le zinc avec l'acide sulfhydrique. On acidifie le filtrat avec l'acide chlorhydrique, on évapore à sec, on dissout le résidu dans l'éthanol absolu et on précipite l'acide aminé avec la pyridine.

Rendement: 0.5 g. (6%). P.f. 254° à 260°C. (déc.) (capillaire scellé). Calculé pour $C_9H_{11}NO_2$: N, 8.49%. Trouvé: N, 8.54%.

Si l'on applique la même méthode à la phénylhydrazone de l'acide phénylpyruvique, on obtient un rendement brut de 97%.

D. On porte à reflux pendant 24 h., un mélange d'acide acétique à 75% (150 ml.), de zinc (14 g., 0.24 mole) et de phénylhydrazone d'acide phénylpyruvique (10 g., 0.0394 mole). Pendant ce temps, la solution devient blanche ou limpide. On décante alors de l'excès de zinc, et on évapore à sec. On ajoute 150 ml. d'eau au résidu, on filtre si nécessaire, on précipite le zinc par l'hydrogène sulfuré et on porte à ébullition la solution avant de filtrer. On évapore le filtrat à sec, on ajoute de l'éthanol au résidu, on filtre et on lave avec de

l'éthanol et de l'eau. Rendement: 3.4 g. (53%). P.f. 236° à 242°C. (capillaire scellé). Calculé pour $C_9H_{11}NO_2$: N, 8.49%. Trouvé: N, 8.48%.

On peut préparer d'une façon analogue:

L'O-méthyltyrosine (de la phénylhydrazone correspondante). Rendement: 58%. P.f. 252°C. à 255°C. (capillaire scellé). Litt.: 262°C. (13). Calculé pour $C_{10}H_{13}NO_3$: N, 7.18%. Trouvé: N, 7.18%.

L'O-méthyltyrosine (de l'oxime correspondante). Rendement: 26%. P.f. 252° à 255°C. Calculé pour $C_{10}H_{13}NO_3$: N, 7.18%. Trouvé: N, 7.16%.

Le dérivé phényluréidé de l'O-méthyltyrosine cristallise de l'éthanol aqueux en feuilles blanches. P.f. 165° à 165.5°C. Calculé pour $C_{17}H_{19}O_4N_2$: N, 8.91%. Trouvé: N, 8.94%.

Le dérivé phényluréidé fut ensuite cyclisé en 3-phényl-5-anisylhydantoïne par l'action de l'acide chlorhydrique. Il se forme une poudre blanche de l'éthanol aqueux. P.f. 159° à 160°C. Calculé pour $C_{17}H_{19}O_3N_2$: N, 9.46%. Trouvé: N, 9.54%.

dl-Tyrosine. Rendement: 20%. P.f. 293° à 294°C. (capillaire scellé). Calculé pour $C_9H_{11}NO_3$: N, 7.73%. Trouvé: N, 7.75%.

dl-Valine. Rendement: 20%. P.f. 254°C. (capillaire scellé). Calculé pour $C_8H_{11}NO_2$: N, 12.0%. Trouvé: N, 12.0%.

E. On ajoute de l'acide α -oximino- β -phénylpropionique (10 g., 0.055 mole) à un mélange d'éthanol (100 ml.) et d'acide sulfurique à 15% (60 ml.). La cellule électrolytique consiste en un bécber qui contient du mercure d'une surface de 139 cm.², et servant de cathode. L'anode est un filament de platine placé dans une petite coupe poreuse, suspendue dans la solution. L'anolyte est de l'acide sulfurique à 15%. On refroidit la solution à 0–5°C. et on y fait passer un courant de 3 ampères pendant deux heures. On peut isoler l'acide aminé de la solution soit par précipitation au point isoélectrique, soit par neutralisation exacte avec l'hydroxide de barium, filtration et évaporation du filtrat. Rendement: 6.6 g. (82%).

On peut préparer l'O-méthyltyrosine d'une façon analogue. Rendement: 48%. P.f. 258° à 260°C. Litt.: 262°C. (13). Calculé pour $C_{10}H_{13}NO_3$: N, 7.18%. Trouvé: N, 7.14%.

Remerciements

Les auteurs sont heureux de remercier le Conseil National des Recherches du Canada pour l'aide financière qui a permis la réalisation de ce travail. Ils sont aussi redevables au docteur Karl F. Keirstead d'avoir bien voulu effectuer les réductions électrolytiques des oximes.

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CONDUCTANCE MEASUREMENTS IN WATER - NITRIC ACID - NITROGEN PENTOXIDE MIXTURES AT VARIOUS TEMPERATURES¹

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Abstract

Conductance measurements in the system water - nitric acid - nitrogen pentoxide have been made over a range of temperatures. The results are in accordance with the findings of Veley and Manley (12) as regards (1) the presence of a minimum in the specific conductance at about 96% by weight nitric acid (2) the existence of a negative temperature coefficient of specific conductance for solutions rich in nitric acid. As reported by Berl and Saenger (1) the specific conductance of solutions of nitrogen pentoxide in nitric acid at first increases with increasing concentration of the former, ultimately attaining a maximum and then decreasing with further increase in the nitrogen pentoxide content. Some viscosity and density data for nitric acid - nitrogen pentoxide mixtures are included.

Introduction

In recent years the nature of concentrated aqueous solutions of nitric acid has formed the object of many types of experimental investigations. The evidence obtained seems to indicate the presence of nitryl ion (NO_2^+) although it is likely that more complex constituents must be present in order to account for the results thus far observed. The presence of ionic constituents will of course be made evident by conductance measurements. While these alone cannot be expected to elucidate completely this apparently complicated problem it seemed worthwhile to make this type of attack. Furthermore, even allowing for the instability of such systems it is difficult to reconcile the contradictory conductance values reported by various workers.

Veley and Manley (12), on the basis of a carefully planned investigation, reported measurements for 0-100% nitric acid at 0°, 15°, and 30°C. They note the presence of a minimum in the specific conductance at about 96% nitric acid and report a small negative temperature coefficient of conductance for concentrations slightly greater than this value. Hantzsch (5), on the other hand, was unable to confirm the minimum and asserts that at 0°C. the conductance increases steadily as the water content is increased. The work of Berl and Saenger (1), who carried out a rather extensive physicochemical study of the system nitric acid - nitrogen pentoxide and who have reported specific conductances in this system at 18°C. made it clear that a conductance minimum must exist, as Veley and Manley report. The recent publication of

¹ Manuscript received in original form November 3, 1950, and, as revised, February 14, 1951.

Contribution from the Department of Chemistry, Queen's University, Kingston, Ontario. The contents of this paper has been extracted from theses submitted by L. Murray Lyne (1946) and by Alan G. Follows (1945) to Queen's University in partial fulfillment of the requirements for the degrees of Master of Science. Our thanks are due to the Associate Committee on Explosives of the National Research Council of Canada for financial assistance.

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Chanukvadze (3), including a conductance investigation of the system water – nitric acid from 0° to 40°C. at 10° intervals, presents data for lower concentrations which are considerably at variance with those of other workers. Chanukvadze does not include sufficient data to ascertain the form of the conductance curve in the region of the minimum reported by Veley and Manley.

We have determined the specific conductances of water – nitric acid mixtures (0–100% acid) at 25°C. Our results are in substantial agreement with those calculated from the data given by Veley and Manley (see Fig. 1). We have made conductance measurements with mixtures rich in nitric acid and with nitric acid – nitrogen pentoxide mixtures at 0°, 18°, 25° and 40°C. Where comparison is possible our results are in fairly good agreement with those reported by Veley and Manley and by Berl and Saenger (see Figs. 1, 1A, 2 and 3).

In view of the difficulty of avoiding completely decomposition of the nitric acid we have determined the influence of nitrogen tetroxide on the conductance of the solutions. In addition the effect of water on nitric acid – nitrogen tetroxide mixtures has been investigated.

Some density and viscosity determinations have been made because these were not available.

Experimental

Materials

Anhydrous nitric acid was prepared by the distillation of sodium nitrate with 98% sulphuric acid at a pressure of approximately 30 mm. It was analyzed gravimetrically using Iceland spar by a method almost identical with that described by Masson (11). The chloramine-T method (13) was used to determine nitrogen tetroxide in the nitric acid. The anhydrous acid as distilled always contained less than 0.05% nitrogen tetroxide although the solutions rich in nitrogen pentoxide sometimes contained as much as 0.2% nitrogen tetroxide after standing for several hours at room temperature. Solutions of nitrogen pentoxide in nitric acid were prepared in the usual manner by distilling a mixture of phosphorus pentoxide and anhydrous nitric acid at a pressure of about 35 mm. Usually about one half of the yellowish distillate consisted of a solid phase which went into solution after removal from the freezing bath. These mixtures were analyzed either gravimetrically as mentioned above or volumetrically by the addition of excess standard sodium hydroxide solution followed by back-titration with hydrochloric acid using phenol red as indicator. Nitrogen tetroxide was prepared from lead nitrate in the usual manner and redistilled into weighed ampoules which were then sealed off, leaving a thin glass tip which could be easily broken off inside the conductance cell.

Procedure

In runs at constant temperature a weighed amount of the nitric acid or nitric acid – nitrogen pentoxide mixture was placed in the conductance cell

and successive additions of water were made from a Lunge weighing pipette. The cell and contents were cooled in ice water before making the additions so as to minimize decomposition. The above method is not suitable for measurements at elevated temperatures because of decomposition, so that fresh samples of a water - nitric acid or of a nitric acid - nitrogen pentoxide mixture of known composition were placed in the cell for each measurement. Additional experiments were made in which a solution of known composition was placed in the cell and the temperature raised from 0° to 30°C., the conductance being measured at 5° intervals.

In the addition of nitrogen tetroxide to the cell it was found that this substance is so readily soluble in nitric acid mixtures that little loss occurs when the tip of the ampoule is broken off. Density measurements were made using a 25 ml. volumetric flask as a pycnometer. The viscosities were measured in an Ostwald viscometer for which the time of flow of water at 25°C. was about 120 sec. The densities and viscosities are precise to about $\pm 1\%$.

Electrical Measurements

The cells consisted of 250 ml. Erlenmeyer flasks to the bottoms of which were sealed long tubes carrying small platinized electrodes. The cell constants varied between 16 and 60; such high values were necessary because of the high conductances encountered. Electrically controlled oil thermostats (temperatures constant to $\pm 0.02^\circ$) were used for most of the measurements while for those at 0°C. and for those in which the temperature was changed continuously from 0° to 30°C. a water thermostat was employed.

The resistances were measured by means of a direct reading a-c. bridge constructed according to the principles laid down by Jones and Josephs (8). Measurements were made at different frequencies so that polarization effects could be detected and the appropriate corrections applied if necessary (7).

Results

In Table I are presented the specific conductances (κ) of water - nitric acid - nitrogen pentoxide mixtures whose compositions are expressed in mole % total nitrogen pentoxide. The results of 12 separate runs are included together with 16 values obtained on individual nitric acid - nitrogen pentoxide mixtures. The results shown in Table I are plotted in Figs. 1 and 1A together with data calculated from the results of Veley and Manley and of Chanukvadze. In Table II are presented the conductances of water - nitric acid mixtures at 0°C., the results being plotted in Fig. 2 in which the data of Hantzsch and of Chanukvadze are included for comparison. In Table III are presented the conductances of water - nitric acid - nitrogen pentoxide mixtures at 18°C.; the results are plotted in Fig. 3, which shows also data published by Veley and Manley and by Berl and Saenger. In Table IV are recorded the conductances of water - nitric acid - nitrogen pentoxide mixtures at 40°C., the values being plotted in Fig. 4. Table V gives the results of experiments in which the conductances of various single water - nitric acid - nitrogen pentoxide mixtures

were measured at one or more temperatures; the data are plotted in Fig. 5 and the composition of each mixture is recorded on the plots. In Table VI are presented the densities ($D_4^{25^\circ}$) and viscosities of various nitric acid-nitrogen pentoxide mixtures, the values, along with some for water-nitric acid mixtures taken from the literature, being plotted in Fig. 6. In Tables

TABLE I
THE CONDUCTANCE OF WATER - NITRIC ACID - NITROGEN PENTOXIDE MIXTURES AT 25°C.

Mole % N_2O_5	10^2x	Mole % N_2O_5	10^2x
0.03347	1.480	28.27	17.93
0.1049	4.449	32.23	10.45
0.3504	14.00	38.57	4.111
0.8851	32.06	43.63	1.836
1.520	49.15	50.15	3.952
1.486	48.93	41.94	2.284
2.055	60.52	44.51	1.557
2.950	73.32	45.57	1.450
3.825	80.99	46.35	1.473
4.014	81.90	47.14	1.604
4.138	82.72	48.48	2.169
4.306	83.28	48.96	2.508
4.484	83.94	49.47	2.925
4.628	84.50	50.00	3.744
4.226	83.38	50.35	3.366
5.119	85.80	51.42	5.918
5.786	86.22	52.72	10.64
6.913	84.74	54.07	14.25
8.088	81.60		
9.370	77.68	54.86	15.38
11.35	70.95	56.50	16.78
		57.56	16.67
8.619	80.10	58.43	16.27
10.31	74.57	59.54	15.72
12.00	68.98		
14.52	61.23	55.47	16.07
16.60	54.76	57.77	16.94
		60.00	16.16
11.08	71.92		
14.91	59.43		
18.46	48.50		
20.00	43.52	51.06	6.320
		51.61	7.650
12.96	65.76	51.97	9.450
13.85	62.95	52.72	11.99
15.75	57.23	53.29	13.13
17.33	52.31		
20.34	42.34	53.87	14.23
23.54	31.51	53.87	14.27
		54.86	15.75
21.11	39.58	56.71	16.71
23.34	31.87	57.34	16.84
26.51	21.95		
45.57	1.393	57.34	16.84
49.47	3.318	58.43	16.68
		58.43	16.73
		59.09	16.32
		61.39	15.39
		61.39	14.90

TABLE II
THE CONDUCTANCE OF WATER - NITRIC ACID MIXTURES AT 0°C.

Mole % N_2O_5	10^2x
49.84	3.368
48.45	2.118
46.35	1.390
44.36	1.302
42.63	1.578
40.34	2.241
36.47	4.084
31.28	8.513

TABLE III
THE CONDUCTANCES OF WATER - NITRIC ACID - NITROGEN PENTOXIDE MIXTURES AT 18°C.

Mole % N_2O_5	10^2x	Mole % N_2O_5	10^2x
50.16	3.358	50.01	3.703
47.65	1.674	49.81	3.102
46.32	1.403	48.96	2.473
45.70	1.386	48.65	2.314
45.24	1.400	48.10	1.928
43.64	1.651	46.80	1.509
39.40	3.338	45.59	1.400
		44.36	1.497
		41.81	2.192
		40.75	2.602
59.54	14.11	54.07	13.30
58.43	14.69	52.72	9.995
57.56	15.17	51.42	5.711
56.50	15.42	50.35	3.379
54.86	14.26		

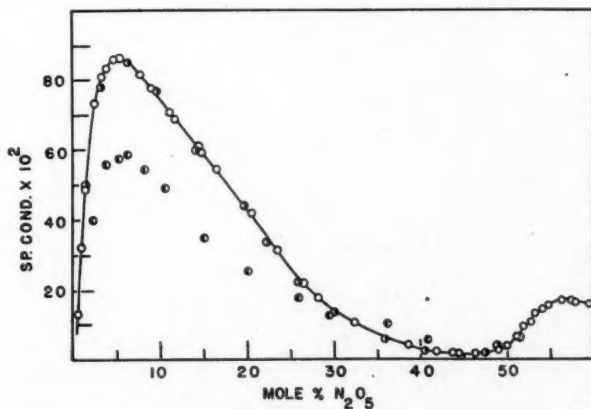


FIG. 1. The conductance of water - nitric acid - nitrogen pentoxide mixtures at 25°C. ○ Present investigation; ● Veley and Manley (interpolated); ◐ Chanukvadze (interpolated).

VII and VIII are presented results showing the effect of nitrogen tetroxide on the conductance of anhydrous nitric acid and on that of a nitric acid - nitrogen pentoxide mixture respectively; the results are illustrated graphically in Fig. 7. Tables IX and X give the results of adding water to nitric acid and to nitric acid - nitrogen pentoxide mixture respectively, both containing given amounts of nitrogen tetroxide; the data are plotted in Fig. 8.

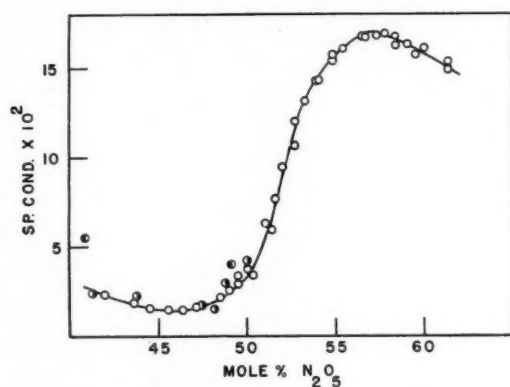


FIG. 1A. The conductance of water - nitric acid - nitrogen pentoxide mixtures (large scale plot of region rich in nitrogen pentoxide) at 25°C. ○ Present investigation; ◐ Veley and Manley (interpolated); ● Chanukvadze (interpolated).

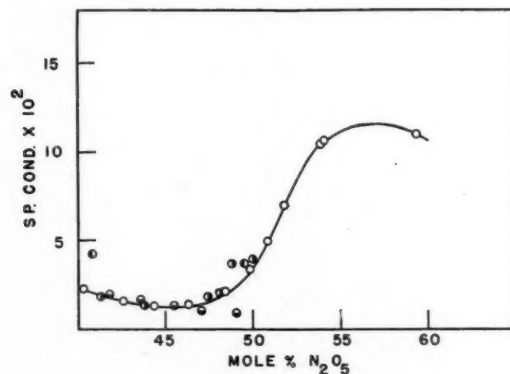


FIG. 2. The conductance of water - nitric acid - nitrogen pentoxide mixtures at 0°C. ○ Present investigation; ◐ Veley and Manley; ● Chanukvadze; ◐ Hantzsch.

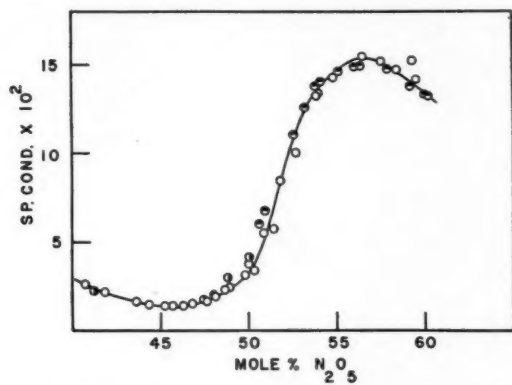


FIG. 3. The conductance of water-nitric acid-nitrogen pentoxide mixtures at 18°C. \odot Present investigation; \bullet Veley and Manley (interpolated); \bullet Berl and Saenger.

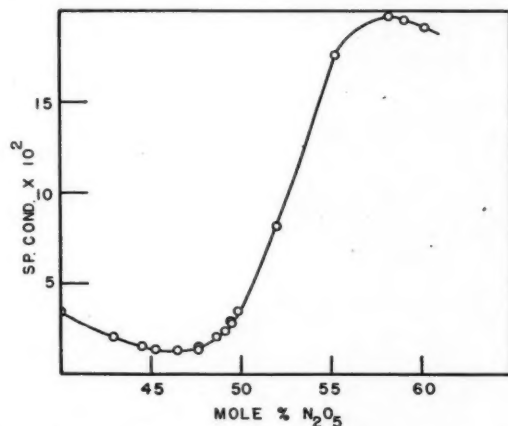


FIG. 4. The conductance of water-nitric acid-nitrogen pentoxide mixtures at 40°C.

TABLE IV

THE CONDUCTANCE OF WATER-NITRIC ACID-NITROGEN PENTOXIDE MIXTURES AT 40°C.

Mole % N_2O_5	10^2x	Mole % N_2O_5	10^2x
60.22	19.11	49.84	3.453
59.09	19.54	49.48	2.944
58.21	19.73	48.62	2.042
55.26	17.58	47.64	1.555
51.97	8.166	46.48	1.332
		45.26	1.375
49.97	3.462	44.50	1.544
49.47	2.778	42.89	2.058
49.12	2.330	40.06	3.439
47.63	1.560		

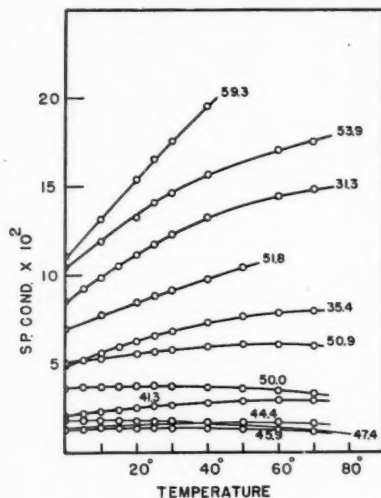


FIG. 5. The variation of conductance with temperature for various water - nitric acid - nitrogen pentoxide mixtures.

TABLE V

THE CONDUCTANCE OF WATER - NITRIC ACID - NITROGEN PENTOXIDE MIXTURES AT VARIOUS TEMPERATURES

Mole % N_2O_5	31.28	35.44	41.26	44.36	45.88	47.44
Temperature, $^{\circ}C$.	Specific conductance $\times 10^2$					
0	8.513	4.840	2.020	1.360	1.288	1.789
5	9.212	5.187	2.150	1.418	1.295	1.778
10	9.835	5.560	2.269	1.470	1.311	1.765
15	10.55	5.918	2.380	1.520	1.322	1.745
20	11.19	6.250	2.485	1.562	1.328	1.720
25	11.74	6.552	2.578	1.596	1.330	1.686
30	12.30	6.813	2.659	1.623	1.328	1.652
40	13.25	7.323	2.796	1.671	1.313	1.579
50		7.637	2.865	1.683	1.282	1.483
60	14.47	7.892	2.910	1.672	1.248	1.395
70	14.80	7.962	2.884	1.638	1.190	1.26
Mole % N_2O_5	50.00	50.86	51.79	53.87	54.07	59.32
Temperature, $^{\circ}C$.	Specific conductance $\times 10^2$					
0	3.558	4.931	6.986	10.47	10.63	11.05
5	3.615	—	—	—	—	—
10	3.653	5.262	7.735	11.90	12.15	13.11
15	3.678	—	—	—	—	—
20	3.701	5.551	8.482	13.29	13.63	15.34
25	3.704	5.674	8.840	14.10	14.36	16.51
30	3.690	5.766	9.132	14.63	14.99	17.54
40	3.638	5.952	9.770	15.69	16.22	19.5
50	3.541	6.075	—	—	—	—
60	3.419	6.070	10.47	17.02	17.49	—
70	3.240	5.968	—	17.5	—	—

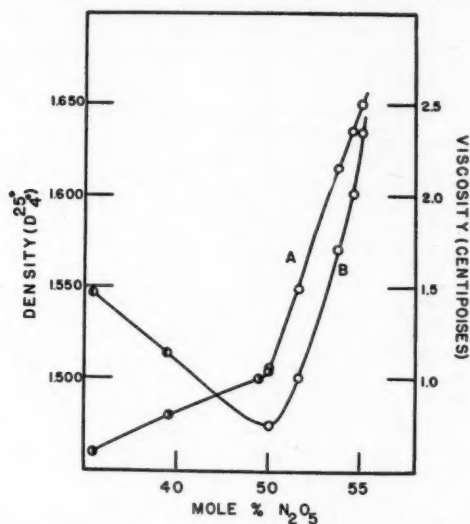


FIG. 6. The density and viscosity of water - nitric acid - nitrogen pentoxide mixtures at 25°C. Curve A: Densities (left hand scale); \odot present investigation; \bullet interpolated from data given in International Critical Tables (6). Curve B: Viscosities (right hand scale); \odot present investigation; \bullet Bingham and Stone (2).

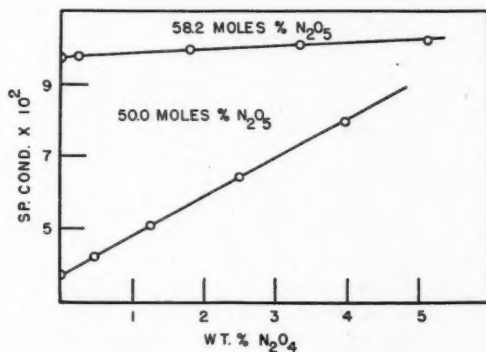


FIG. 7. The effect of nitrogen tetroxide on the conductance of nitric acid - nitrogen pentoxide mixtures at 25°C.

TABLE VI

DENSITIES AND VISCOSITIES OF NITRIC ACID - NITROGEN PENTOXIDE MIXTURES AT 25°C.

Mole % N ₂ O ₅	Density (d_4^{25})	Viscosity, centipoises
60.2	1.65	2.35
59.1	1.64	2.02
57.6	1.62	1.71
53.3	1.55	1.01
50.2	1.51	0.745

TABLE VII

THE CONDUCTANCE OF NITROGEN TETROXIDE IN ANHYDROUS NITRIC ACID AT 25°C.

Weight % N_2O_4	10^3x
0.00	3.735
0.469	4.231
1.260	5.098
2.500	6.428
3.986	7.958

TABLE VIII

THE CONDUCTANCE OF NITROGEN TETROXIDE IN A NITRIC ACID - NITROGEN PENTOXIDE MIXTURE CONTAINING 58.43 MOLE % N_2O_5 AT 25°C.

Weight % N_2O_4	10^3x
0.00	16.73
0.251	16.78
1.81	16.93
3.35	17.07
5.14	17.19

TABLE IX

THE EFFECT OF ADDING WATER TO ANHYDROUS NITRIC ACID CONTAINING 4.38% BY WEIGHT OF NITROGEN TETROXIDE AT 25°C.

Weight % H_2O	10^3x
0.00	7.889
0.643	7.088
1.617	6.452
2.785	6.260
3.79	6.32
5.19	6.63
7.15	7.46

TABLE X

THE EFFECT OF ADDING WATER TO NITRIC ACID - NITROGEN PENTOXIDE (58.4 MOLE % N_2O_5) CONTAINING 5.14% NITROGEN TETROXIDE AT 25°C.

Weight % H_2O	10^3x
0.00	17.25
1.122	17.81
2.234	15.80
3.670	10.14
5.67	8.863
7.72	8.715
10.71	9.515
15.41	13.28

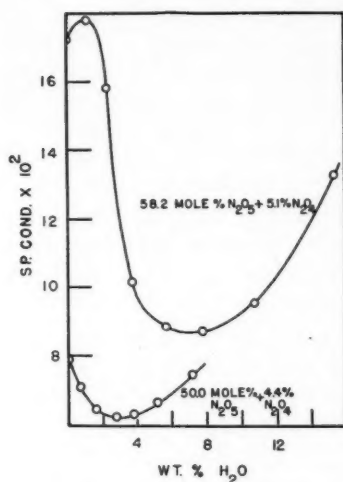
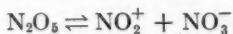


FIG. 8. The effect of water on the conductance of nitric acid - nitrogen pentoxide - nitrogen tetroxide mixtures at 25°C.

Discussion

It appears, in accordance with the earlier findings of Veley and Manley and of Berl and Saenger, that the variation of the specific conductance of water - nitric acid - nitrogen pentoxide mixtures with composition is fairly complex. The form of the curve (Fig. 1) is not unlike that for water - sulphuric acid - sulphur trioxide systems (10) although the sulphur system shows a somewhat more complicated behavior, probably because of a more complex ionization of the acid. The conductance maximum observed at about 30% by weight nitric acid (5.5 mole % N₂O₅) is in the same region of weight concentration as those found for other aqueous systems, in which its occurrence has been attributed to ionic hydration phenomena (4). The decrease in the conductance following the initial maximum must be due in part to an increase in viscosity for at 25°C. the viscosity-concentration curve for water - nitric acid passes through a maximum at approximately 70% nitric acid (20 mole % N₂O₅). However, large interionic forces are undoubtedly responsible for the major portion of the decrease. Calculation shows that the equivalent conductance falls to a value of about 0.6 at the minimum following which it rises to about 1.6 at 100% nitric acid. It thus appears that at approximately 97.5% nitric acid (46 mole % N₂O₅) some highly conducting species must be forming in appreciable quantity. That no sharp break is evident in the conductance curve at 100% nitric acid seems to indicate that the newly formed ionic species may be closely related to nitrogen pentoxide. In conformity with recent ideas (9) it is not unlikely that the nitryl ion (NO₂⁺) is involved. From this it is but a short step to the assumption that nitrogen pentoxide may ionize thus:



On this basis, calculations of the equivalent conductance at 25°C. of nitrogen pentoxide in anhydrous nitric acid as the solvent yield values of from 40 to 50 mhos (the solvent conductance being subtracted from the total conductance to get the true specific conductance of the nitrogen pentoxide) for concentrations of from 0.4 to 3.6 equivalents per liter. These values are not unreasonable although it is realized that the treatment is somewhat arbitrary especially in view of the high solvent conductance.

The effect of temperature on the conductance of various water-nitric acid-nitrogen pentoxide mixtures (Fig. 5) is of considerable interest in throwing light on the nature of the system in the neighborhood of the minimum (45.9 mole % nitrogen pentoxide).

It is striking that for concentrations around this point the conductance varies little with temperature while on either side of the minimum the variation is appreciable. Perhaps a more illustrative picture of the situation is given by Fig. 9 in which the temperature coefficients of specific conductance

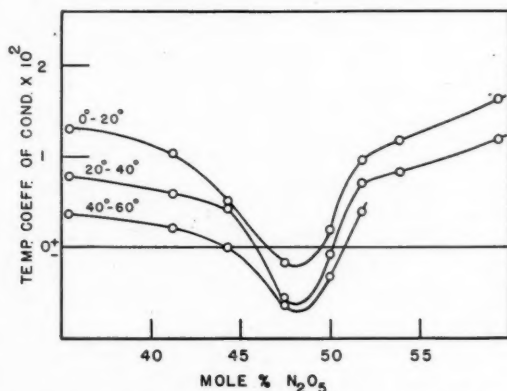
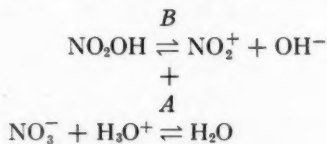


FIG. 9. The temperature coefficients of conductance ($1/\kappa \cdot \Delta\kappa/\Delta t$) of various water-nitric acid-nitrogen pentoxide mixtures.

($1/\kappa \cdot \Delta\kappa/\Delta T$) have been plotted against mole % nitrogen pentoxide. Here it is clearly brought out that approximately between the minimum in the conductance curve and 100% nitric acid the conductance decreases with increasing temperature. It is in this range we have concluded that some new conducting species is being formed in quantity. Presumably the effect of raising the temperature is to oppose this change, which is probably concerned in some manner with the presence of water. The following simple equilibria may be relevant:



We may conjecture that the nitric acid molecule possesses a dual character; the pure acid ionizes as in *B*, while, upon addition of water, equilibrium *A* comes into play. The effect of temperature on these two equilibria, the one involving a simple ionization and the other an ionization following a reaction with water, might well be expected to be complex. Some information on this point could doubtless be obtained by an investigation of ultraviolet, infrared, and Raman spectra at different temperatures. In all probability the system we are dealing with between the minimum in the conductance curve and 100% nitric acid consists essentially of equilibrium *B* and it is well known that the degree of ionization of weak electrolytes may be decreased by increasing temperature. In addition it is probable that equilibrium *A* is shifted towards the left with increasing temperature since it may be seen from Figs. 1A, 2, 3, and 4 that a slight shift in the conductance minimum from 45 mole % to 46.5 mole % nitrogen pentoxide occurs between 0° and 40°C.

For solutions of nitrogen pentoxide in nitric acid we can expect a positive temperature coefficient of conductance. The conductance maximum which appears at 57 mole % nitrogen pentoxide is doubtless due in large measure to the appreciable increase in the viscosity (Fig. 6).

The chemical instability of systems rich in nitrogen pentoxide prompted us to investigate the influence of nitrogen tetroxide on the conductance property. Fig. 7 shows that for anhydrous nitric acid the conductance is a linear function of the weight % nitrogen tetroxide, at least, for low concentrations of the latter. The effect on the conductance is large, 1/10% nitrogen tetroxide raising the conductance from 3.73×10^{-2} to 3.8×10^{-2} . Since water may also be present we have determined the influence of water on the conductance of anhydrous nitric acid containing nitrogen tetroxide. It should be noted that owing to the opposite effects of nitrogen tetroxide and water on the conductance, a conductimetric analysis of water - nitric acid mixtures (using, say, Fig. 1A) may be in error, owing to mutual cancellation of the effects of such impurities. In Fig. 7 it is shown that the effect of nitrogen tetroxide on the conductance of nitric acid - nitrogen pentoxide mixtures rich in the latter is comparatively small. This fact is fortunate, since it is in these mixtures that small amounts of nitrogen tetroxide are unavoidably present.

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CONDUCTANCE OF AMMONIUM NITRATE IN WATER - NITRIC ACID - NITROGEN PENTOXIDE MIXTURES AT VARIOUS TEMPERATURES¹

BY EDWARD G. TAYLOR,² CHARLES A. N. BAKER, AND L. MURRAY LYNE

Abstract

Conductance measurements have been made with ammonium nitrate in water - nitric acid - nitrogen pentoxide mixtures at various temperatures and over a wide range of concentrations. For all solutions except those rich in nitrogen pentoxide the variation of the specific conductance with the concentration of ammonium nitrate is similar to that observed for many electrolytes in a variety of solvents. With nitrogen-pentoxide-rich solvents however the specific conductance of ammonium nitrate is observed to decrease with increasing salt concentration. This is regarded as indicative of an interaction between the salt and one or more of the components of the nitric acid - nitrogen pentoxide system. The variation of conductance with temperature is normal in all cases. It is shown that ammonium nitrate confers a considerable degree of thermal stability on anhydrous nitric acid.

Introduction

In connection with certain physicochemical studies of various components of the Cyclonite reaction mixture it appeared of interest to carry out conductance measurements with ammonium nitrate in nitric acid and related mixtures. The first reported conductance measurements with this salt in nitric acid (99.4%) were made by Bouty (1) who showed that at 0°C. the solutions were comparatively good conductors. Results are also given for sodium, potassium, rubidium, and thallous nitrates. However, the few data recorded are for relatively low concentrations, although Bouty does remark that as the proportion of alkali metal nitrate is increased the conductance at first increases rapidly, attains a maximum, and then decreases. At the maximum and beyond, the solutions are quite viscous. More recently, Jander and Wendt (2) measured the conductances of several inorganic nitrates in anhydrous nitric acid but here again the measurements have been confined to relatively dilute solutions.

We have measured (1) the conductance of ammonium nitrate in various water - nitric acid - nitrogen pentoxide mixtures at 25°C., (2) the conductance of ammonium nitrate in 100% nitric acid at 25°, 40°, 50°, 60°, and 70°C. It has been shown that, if conductance is any criterion, concentrated solutions of ammonium nitrate are extremely stable as compared with the pure acid.

¹ Manuscript received in original form November 3, 1950, and, as revised February 14, 1951. Contribution from the Department of Chemistry, Queen's University, Kingston, Ontario. The contents of this paper has been extracted from theses submitted by Charles A. N. Baker (1946) and by L. Murray Lyne (1946) to Queen's University in partial fulfillment of the requirements for the degrees of Master of Science. Our thanks are due to the Associate Committee on Explosives of the National Research Council of Canada for financial assistance.

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Experimental

The ammonium nitrate was of reagent grade and was powdered and dried *in vacuo* over phosphorus pentoxide before use. The salt was added to the cell from a weighed stoppered glass bottle. Otherwise the experimental details are the same as those described in an earlier paper (4). It was noted that while heat evolution occurred during the solution of ammonium nitrate in 100% nitric acid or lesser concentrations of the latter, heat absorption took place when ammonium nitrate was added to nitric acid containing free nitrogen pentoxide. When the ammonium nitrate content was high and when mixtures rich in nitrogen pentoxide were studied, sufficient gassing (nitrogen tetroxide) occurred at the electrodes to make resistance readings difficult. This is the reason for failure to extend our measurements to high concentrations of ammonium nitrate in nitric acid containing large amounts of free nitrogen pentoxide. It was further noted that if the nitric acid used was slightly yellow, the addition of ammonium nitrate resulted in the production of a colorless solution. When these solutions were kept for as long as three days in the cell, small bubbles of gas formed in the electrode chamber, yet the conductance of the solution remained virtually unchanged over the entire period (care was of course taken to ensure that no bubbles remained in the electrode chamber during a resistance measurement). Certain solutions of high ammonium nitrate content failed to wet the glass walls of the cell properly. We believe, in spite of these possible sources of error, that our results are precise to ± 1 or 2% or better.

Results

In Table I are presented the specific conductance (κ -in mhos) and mole % concentration of ammonium nitrate in various water-nitric acid mixtures at 25°C. The results have been plotted in Figs. 1 and 2. Table II gives data showing the effect of nitrogen tetroxide on the specific conductance of am-

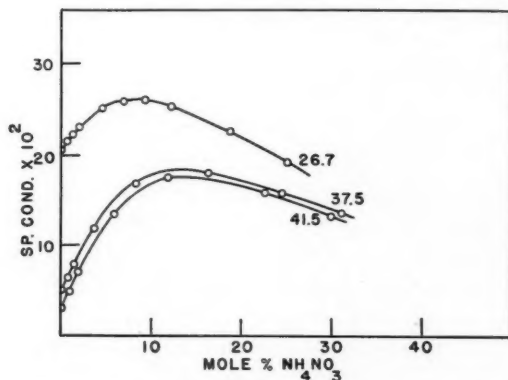


FIG. 1. The conductance of ammonium nitrate in water-nitric acid mixtures at 25° (on this and other figures the values refer to the mole % total nitrogen pentoxide of the solvent).

monium nitrate in 100% nitric acid at 25°C.; the data are plotted in Fig. 2 (Curve A).

In Table III are presented the specific conductance (κ) for ammonium nitrate in 100% nitric acid at various temperatures: these data are shown graphically in Fig. 3. Table IV gives the results of heating under reflux a concentrated solution of ammonium nitrate in 100% nitric acid for successive one hour periods at three temperatures. In Table V are presented the specific

TABLE I

THE CONDUCTANCE OF AMMONIUM NITRATE IN VARIOUS WATER - NITRIC ACID MIXTURES AT 25°C.

Mole % NH_4NO_3	$10^3\kappa$	Mole % NH_4NO_3	$10^3\kappa$
<i>A. 26.6 mole % N_2O_5</i>		<i>B. 37.48 mole % N_2O_5</i>	
0.000	20.54	0.000	5.090
0.644	21.50	0.6619	6.408
1.283	22.25	1.368	7.842
1.977	23.04	3.595	11.87
4.475	25.10	8.280	16.84
6.945	25.96	16.33	18.06
9.293	26.04	24.41	15.85
12.20	25.39	31.04	13.61
18.67	22.75		
24.97	19.25		
<i>C. 41.53 mole % N_2O_5</i>		<i>D. 44.95 mole % N_2O_5</i>	
0.000	3.019	0.000	1.527
0.8621	4.920	1.545	5.330
1.844	7.102	3.400	9.377
5.845	13.46	9.570	16.57
11.82	17.55	15.81	17.68
22.55	15.94	23.96	15.30
29.97	13.35	31.97	12.27
<i>E. 50.00 mole % N_2O_5</i>			
0.000	3.865	0.000	3.730
0.7973	5.743	1.204	6.146
1.620	7.129	2.582	8.830
4.627	12.41	5.452	13.46
9.883	17.74	10.51	18.10
16.41	18.73	19.98	17.76
22.22	16.75	29.00	13.79
31.48	12.72	36.68	10.68
38.84	10.00	43.27	8.566
49.30	7.078		
0.000	3.300	25.88	15.17
31.08	12.90	34.14	11.64
34.07	11.79	39.53	9.683
37.24	10.56	44.88	8.066
41.73	9.080		
45.58	7.968		
48.82	7.109		

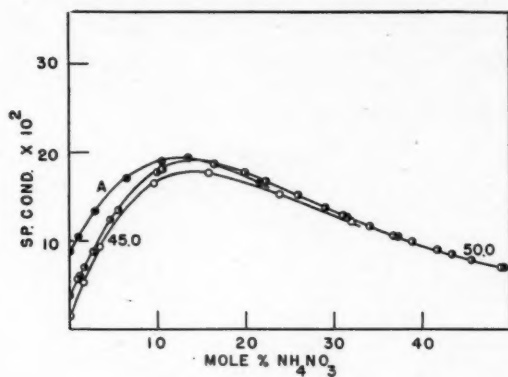


FIG. 2. The conductance of ammonium nitrate in water-nitric acid mixtures at 25°C.; Curve A is for a 50 mole % total nitrogen pentoxide solvent containing 5.0% by weight of nitrogen tetroxide.

TABLE II

CONDUCTANCE OF AMMONIUM NITRATE IN 100% NITRIC ACID CONTAINING 5.00% BY WEIGHT OF NITROGEN TETROXIDE AT 25°C.

Mole % NH_4NO_3	$10^2\kappa$
0.000	8.940
0.9474	10.48
2.901	13.35
6.448	17.11
10.45	18.98
13.39	19.28
16.47	18.68
21.59	16.73

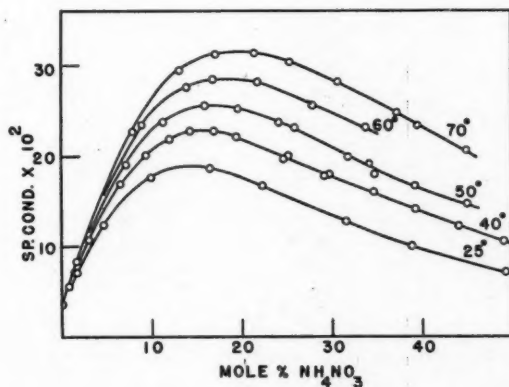


FIG. 3. The conductance of ammonium nitrate in anhydrous nitric acid at various temperatures.

conductance of ammonium nitrate in nitric acid – nitrogen pentoxide mixtures at 25°C.; the results are plotted in Figs. 4 and 5. Finally in Table VI are recorded density and viscosity data for two solutions of ammonium nitrate in nitric acid – nitrogen pentoxide mixtures at 25°C.

TABLE III
CONDUCTANCE OF AMMONIUM NITRATE IN 100% NITRIC ACID AT VARIOUS TEMPERATURES

Mole % NH_4NO_3	$10^3\kappa$	Mole % NH_4NO_3	$10^3\kappa$
<i>A. Temperature, 40°C.</i>			
0.000	3.732	0.000	3.868
0.7744	5.616	25.11	20.12
2.965	10.74	29.74	18.11
6.474	16.93	34.48	16.02
9.263	20.15	39.18	14.01
11.95	21.89	44.00	12.24
14.21	22.65	49.06	10.57
16.90	22.71	54.13	9.75
19.35	22.18		
24.55	19.73		
29.14	17.80		
<i>B. Temperature, 50°C.</i>			
0.000	3.332	25.88	23.18
1.378	7.026	34.14	19.22
7.077	19.05	39.06	16.79
11.23	23.68	44.88	14.66
15.88	25.51		
19.58	25.16		
24.07	23.65		
31.72	19.88		
34.59	18.02		
<i>C. Temperature, 60°C.</i>			
0.000	3.481		
1.631	8.347		
8.915	23.38		
13.85	27.46		
16.78	28.44		
21.71	28.13		
27.83	25.52		
33.71	23.18		
<i>D. Temperature, 70°C.</i>			
0.000	3.397	39.50	23.35
1.369	7.588	44.88	20.62
7.927	22.67		
13.10	29.26		
17.07	31.07		
21.39	31.27		
25.28	30.27		
30.59	28.06		
37.13	24.78		

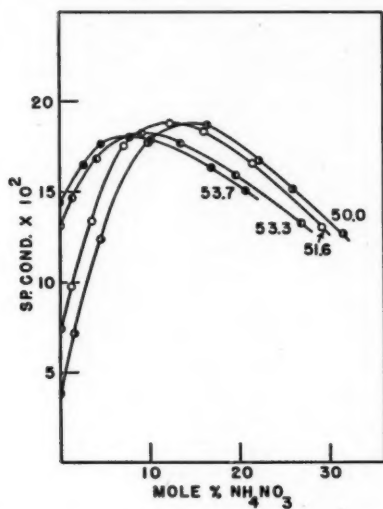


FIG. 4. The conductance of ammonium nitrate in nitric acid - nitrogen pentoxide mixtures at 25°C.

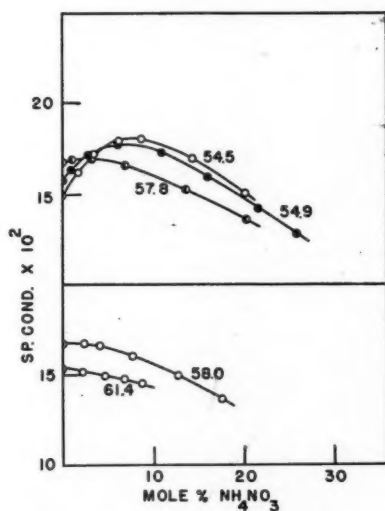


FIG. 5. The conductance of ammonium nitrate in nitric acid - nitrogen pentoxide mixtures at 25°C.

TABLE IV

CONDUCTANCE OF A SOLUTION OF AMMONIUM NITRATE (34.03 mole %) IN 100% NITRIC ACID, BEFORE AND AFTER HEATING UNDER REFLUX FOR ONE HOUR

Temperature of heating, °C.	Initial conductance (25°C.) 10 ³ k	Final conductance (25°C.) 10 ³ k
60	12.45	12.59
80	12.59	12.62
100	12.62	12.60

TABLE V

CONDUCTANCE OF AMMONIUM NITRATE IN NITRIC ACID - NITROGEN PENTOXIDE MIXTURES AT 25°C.

Mole % NH ₄ NO ₃	10 ³ k	Mole % NH ₄ NO ₃	10 ³ k
<i>A. 51.61 mole % N₂O₅</i>		<i>B. 53.3 mole % N₂O₅</i>	
0.000	7.370	0.000	13.13
1.258	9.713	1.400	14.68
3.600	13.38	4.184	16.83
8.139	17.55	9.151	18.28
12.34	18.73	13.53	17.73
16.12	18.33	19.57	15.94
21.42	16.57	26.82	13.31
29.11	13.08		
<i>C. 53.68 mole % N₂O₅</i>		<i>D. 54.46 mole % N₂O₅</i>	
0.000	14.41	0.000	14.90
2.681	16.48	1.715	16.20
4.597	17.62	3.512	17.21
7.862	18.02	6.231	17.91
10.17	17.93	8.684	18.02
16.85	16.32	14.30	16.98
20.72	15.08	20.17	15.06
<i>E. 54.86 mole % N₂O₅</i>		<i>F. 57.78 mole % N₂O₅</i>	
0.000	15.75	0.000	16.76
0.9543	16.34	0.9459	16.92
2.795	17.13	3.143	16.98
6.149	17.73	6.870	16.60
10.98	17.33	13.56	15.24
16.04	15.98	20.28	13.60
21.59	14.20		
25.86	12.84		
<i>G. 58.0 mole % N₂O₅</i>		<i>H. 61.4 mole % N₂O₅</i>	
0.000	16.73	0.000	15.35
2.334	16.74	2.100	15.15
4.036	16.61	4.525	14.93
7.688	16.04	6.694	14.73
12.58	14.96	8.734	14.53
17.51	13.67		

TABLE VI

DENSITIES AND VISCOSITIES OF SOLUTIONS OF AMMONIUM NITRATE IN NITRIC ACID - NITROGEN PENTOXIDE MIXTURES AT 25°C.

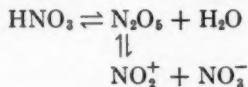
Mole % N ₂ O ₅	Mole % NH ₄ NO ₃	Density ($d_{4}^{25^{\circ}}$)	Viscosity (centipoises)
53.68	0.000	1.558	1.060
53.68	20.72	1.580	4.27
58.00	0.000	1.620	1.553
58.00	17.08	1.594	3.88

Discussion

Figs. 1, 2, and 3 show that ammonium nitrate is a normal electrolyte over the concentration and temperature ranges we have investigated. The usual maximum appears in the conductance-concentration curves, and it may be noted that it is shifted towards higher concentrations of ammonium nitrate as the temperature is increased. Undoubtedly the increasing viscosity is an important factor in causing this behavior. Calculation of the equivalent conductance of ammonium nitrate in anhydrous nitric acid at 25°C. gives values of 85 mhos at about 0.2 *N* and 76 mhos at about 1.3 *N*. Owing to the high solvent conductance it seems pointless to explore these values further but it may be remarked that such values are quite reasonable in comparison with those found in water for the same salt.

The effect of ammonium nitrate in stabilizing nitric acid towards the action of heat is remarkable (see Table IV).

As seen from Figs. 4 and 5, the presence of free nitrogen pentoxide in the nitric acid exerts an appreciable effect on the conductance increment due to added ammonium nitrate. The increased viscosity (Table VI) may be partly responsible for the large diminution in the extent to which ammonium nitrate raises the conductance of nitric acid - nitrogen pentoxide mixtures. It is however difficult to understand why the conductance of a solution containing 61.4 mole % nitrogen pentoxide falls almost continuously as ammonium nitrate is added (See Fig. 5). Possibly a repression of the ionization of the free nitrogen pentoxide is partly responsible for the effects observed. The formation of molecular nitrogen pentoxide may be the reason for the extreme instability noted for these systems. The apparent stabilization of 100% nitric acid by ammonium nitrate may be explained thus:

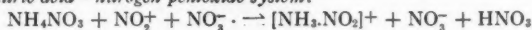


At any rate it seems plausible that these two phenomena are somehow related although it must be admitted that in the absence of additional data these hypotheses are largely speculative.*

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* One of the referees has suggested the following as the mode of interaction of ammonium nitrate with the nitric acid - nitrogen pentoxide system:



The $[\text{NH}_3\text{NO}_2]^+$ ion is suggested as the ammono analogue of the nitracidium ion. We had previously envisaged such an interaction but, because of the similarity in the ultraviolet absorption spectra of potassium and ammonium nitrates in anhydrous nitric acid (3) and because the conductance curves for the two salts are quite similar (5), we had decided that the ammonium ion offered no specific interaction possibilities. However, because of the specificity of ammonium nitrate in the Cyclonite reaction mixture such a suggestion is certainly plausible in the absence of further information.

SOME FREEZING POINT AND CONDUCTANCE MEASUREMENTS IN THE SYSTEM NITRIC ACID - ACETIC ACID¹

BY EDWARD G. TAYLOR² AND ALAN G. FOLLOWS

Abstract

An independent investigation of the phase diagram for the solid-liquid system nitric acid - acetic acid has confirmed the findings of Miskidzh'yan and Trifonov (4), namely, that a 1:1 molecular compound exists. Conductance measurements at 0°, 25°, and 40°C. have been made for the same system. It does not appear possible to predict compound formation from the conductance measurements alone. A preliminary investigation of the liquid-vapor equilibrium for the system nitric acid - acetic acid indicates the existence of a maximum boiling azeotrope. Diacetylorthonitric acid— $(\text{CH}_3\text{COO})_2\text{N}(\text{OH})$ —discovered by Pictet and Genequand (8) is, in all probability, identical with this binary azeotrope. Some molecular weight measurements tend to confirm this view.

Introduction

The investigation of the properties of nitric acid - acetic acid systems is of importance in connection with nitration processes. To this end Briner, Susz, and Favarger (1) carried out Raman spectra, viscosity, and freezing point measurements in this system. From their results they concluded the existence of a loose addition compound composed of one molecule of each acid. A detailed solid-liquid phase diagram cannot be drawn on the basis of the sketchy data (see Fig. 1) reported and it was deemed desirable to obtain more points for this purpose. In addition we decided to measure the conductances of nitric acid - acetic acid mixtures over a wide range of concentrations at 0°, 25°, and 40°C. Subsequent to the completion of the present investigation Miskidzh'yan and Trifonov in 1947 (4) (6) and Naumova in 1949 (7) reported density, viscosity, conductance, and freezing point measurements for this system. Miskidzh'yan and Trifonov report a rather large change in conductance with time, and some of their data together with those of Naumova differ from ours (see Figs. 2 and 3). While we have noticed a change of conductance with time, it is small—averaging about 0.2% per hour—and in view of the time taken for a run we estimate our precision to be $\pm 1\%$ or better. Furthermore, almost all of our points obtained in independent runs lie on the same smooth curve for the same temperature. We have therefore reported our conductance data for 0° and 25°C. as well as those at 40°C. for which no data are available. In determining the freezing point curve for the nitric acid - acetic acid system we have found that the results reported by Briner *et al.* differ somewhat from ours, which are in excellent agreement with those obtained by Miskidzh'yan and Trifonov.

¹ Manuscript received in original form November 3, 1950, and, as revised February 14, 1951.

Contribution from the Department of Chemistry, Queen's University, Kingston, Ontario. The contents of this paper has been extracted from a thesis submitted by Alan G. Follows in 1945 to Queen's University in partial fulfillment of the requirements for the degree of Master of Science. Our thanks are due to the Associate Committee on Explosives of the National Research Council for financial assistance.

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Experimental

Materials

Anhydrous nitric acid was prepared as described in an earlier paper (10). Acetic acid (commercial grade, m.p. 16.47°C.) was two-thirds frozen and after removal of the liquid phase the remainder was distilled over anhydrous calcium sulphate using a 20 in. Vigreux column. The middle fraction (about 50%), which was used in the measurements, possessed a specific conductance of about 1×10^{-8} mhos; its melting point was 16.60°C.

Carbon tetrachloride, used in calibrating the thermometer, was purified by successive washings with concentrated sulphuric acid, water, aqueous potassium hydroxide, and water, followed by distillation after drying over calcium chloride.

Procedure

The freezing point measurements were made in a simple Beckmann apparatus using dry ice and alcohol as the freezing mixture. A pentane thermometer (range +35° to -135°C.) calibrated against the melting points of carbon tetrachloride [-22.85°C.(11)] and of anhydrous nitric acid (-41.5°C.(3)) was used. Melting points were determined by the thaw-melt method of Rheinboldt, Hennig, and Kircheisen (9), and are believed precise to $\pm 0.2^\circ\text{C}$.

For the conductance runs acetic acid was added to the nitric acid in the cell by means of a Lunge weighing pipette. Cooling of the nitric acid was undertaken in order to minimize decomposition due to the heat evolved when the liquids are mixed. The details of the electrical measurements have been given in an earlier paper (10).

Results

A. Freezing Point Measurements

In Table I are presented the melting points of various nitric acid - acetic acid mixtures. The data are plotted in Fig. 1, on which the data of Briner,

TABLE I
THE MELTING POINTS OF NITRIC ACID - ACETIC ACID MIXTURES

Mole % HNO_3	Melting point, $^\circ\text{C}$.
0.000	16.6
19.55	- 6.8
27.12	-24.9
32.57	-41.1
40.42	-30.0
49.43	-24.7
49.84	-23.9
61.72	-30.6
70.45	-45.9
86.74	-49.9
100.0	(-41.6)

Susz, and Favarger, and those of Miskidzh'yan and Trifonov are included for comparison.

B. Conductance Measurements

In Tables II, III, and IV are presented the conductances of nitric acid - acetic acid mixtures at 0°, 25°, and 40°C. respectively, together with the concentrations of the solutions expressed in mole % acetic acid. The results of at least three independent runs are reported. The data are plotted in Figs. 2, 3 and 4, on which are also included data obtained by Miskidzh'yan and Trifonov and by Naumova for purposes of comparison.

TABLE II
THE SPECIFIC CONDUCTANCES OF NITRIC ACID - ACETIC ACID MIXTURES AT 0°C.

Mole % CH ₃ COOH	10 ² x	Mole % CH ₃ COOH	10 ² x
0.000	3.593	53.49	0.1279
6.088	2.043	57.73	0.08369
12.28	1.303	61.05	0.05624
16.62	1.005	63.19	0.04705
20.85	0.8629	66.47	0.03186
26.31	0.7285	67.76	0.02668
31.74	0.5895	70.83	0.01826
34.94	0.5069	72.39	0.01479
44.24	0.2797	75.74	0.00906
70.92	0.01815		
72.84	0.01360		
76.12	0.00822		
79.83	0.00448		
83.05	0.00247		

TABLE III
THE SPECIFIC CONDUCTANCES OF NITRIC ACID - ACETIC ACID MIXTURES AT 25°C.

Mole % CH ₃ COOH	10 ² x	Mole % CH ₃ COOH	10 ² x
0.000	3.734	26.86	0.9541
8.150	1.842	30.51	0.8535
14.53	1.289	33.79	0.7535
19.88	1.110	36.08	0.6805
26.37	0.9700	40.70	0.5364
30.98	0.8456	43.27	0.4588
		48.11	0.3316
		52.13	0.2432
49.20	0.3060	74.50	0.02256
53.24	0.2233	85.21	0.003948
57.57	0.1516	92.17	0.000792
62.29	0.09538	94.58	0.000320
66.01	0.06379	97.00	0.0000695
68.20	0.04967		
70.73	0.03621		
73.35	0.02680		
75.30	0.02006		

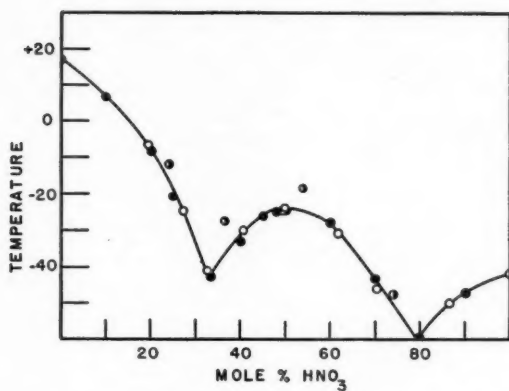


FIG. 1. The melting points of nitric acid-acetic acid mixtures. \circ Present investigation; \bullet Briner, Susz, and Favarger; \bullet Miskidzh'yan and Trifonov.

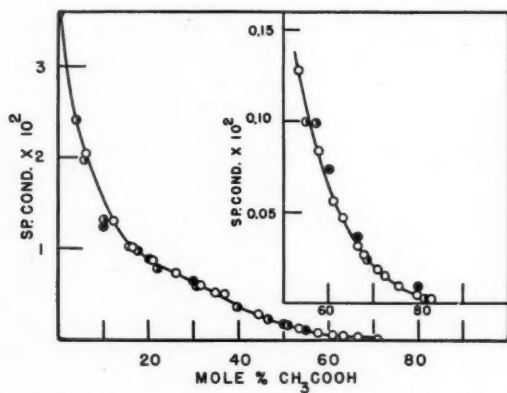


FIG. 2. The conductance of nitric acid-acetic acid mixtures at 0°C . \circ Present investigation; \bullet Miskidzh'yan and Trifonov; \bullet Naumova.

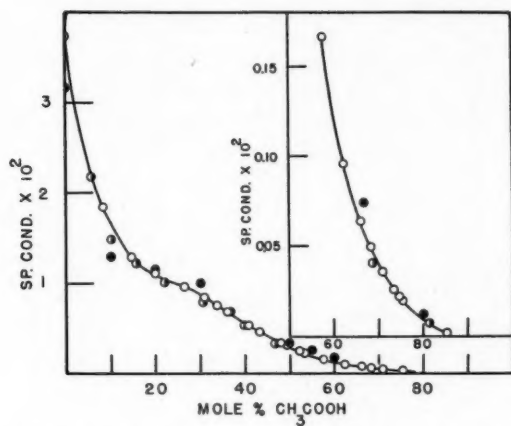


FIG. 3. The conductance of nitric acid-acetic acid mixtures at 25°C. ○ Present investigation; ● Miskidzh'yan and Trifonov; ◐ Naumova.

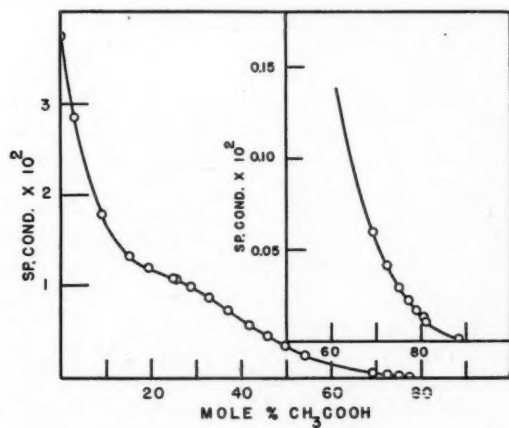


FIG. 4. The conductance of nitric acid-acetic acid mixtures at 40°C.

TABLE IV
THE SPECIFIC CONDUCTANCES OF NITRIC ACID - ACETIC ACID MIXTURES AT 40°C.

Mole % CH ₃ COOH	10 ² x	Mole % CH ₃ COOH	10 ² x
0.000	3.739	25.49	1.064
3.045	2.852	28.81	0.9855
8.996	1.789	32.84	0.8695
15.18	1.322	37.02	0.7372
19.39	1.195	41.70	0.5851
24.94	1.080	45.80	0.4598
		49.81	0.3506
		54.07	0.2533
69.24	0.05987	80.94	0.01069
72.49	0.04118	88.15	0.002865
75.03	0.02963	93.16	0.000696
77.18	0.02222	95.97	0.000234
78.93	0.01681		
80.56	0.01360		

Discussion

A. Freezing Points

As indicated by the data of Briner, Susz, and Favarger, and confirmed by Miskidzh'yan and Trifonov, our results, shown in Fig. 1, point to the existence of a molecular compound—HNO₃·CH₃COOH. No indication is seen of the existence of diacetylorthonitric acid, of which such frequent mention is made throughout the literature following the early work of Pictet and Genequand (8) who reported the discovery of such a compound.

B. Conductances

Based on the ideas of Usanovich and Naumova (12) both Miskidzh'yan and Trifonov and Naumova have attempted to demonstrate the existence of compound formation in solution using plots of the temperature coefficients of conductance ($1/\kappa \cdot \Delta\kappa/\Delta T$) against concentration. Marked changes in the slopes of such curves have been taken as indicative of compound formation. Miskidzh'yan and Trifonov state that for nitric acid - acetic acid mixtures there is a maximum in the plot of temperature coefficient of conductance at about 67 mole % acetic acid. This may be taken as evidence of the compound HNO₃·2CH₃COOH although their interpretation of the mechanism of the interaction between the two acids is then described in terms of the compound HNO₃·CH₃COOH which is formulated as (CH₃COOH₂)⁺(NO₃)⁻. Naumova, on the other hand, notes the appearance of an inflection point at 67 moles % acetic acid which is taken as indicative of HNO₃·2CH₃COOH.

We have calculated temperature coefficients of conductance from our results at 0°, 25°, and 40°C. It appears to us that the temperature coefficient rises steadily from about 1% at 20 mole % acetic acid to about 5% at 80 to 90 mole % acetic acid. To be sure, the curves are somewhat irregular, especially for the 0°-20°C. and 25°-40°C. ranges, but we attribute such discontinuities

to the unavoidable errors in the interpolation from data which are not extremely precise. As justification for this view we find that the curve for the 0°-40°C. range is almost a straight line within the experimental error. In addition it must be remembered that since we are dealing with a difference in conductance, any errors in the actual conductance values are magnified and will cause larger errors percentagewise in the temperature coefficient of conductance. For the nitric acid - acetic acid system at least, it does not appear possible to us to deduce the existence of compound formation on the basis of conductance measurements.

C. Miscellaneous Observations

Viscosity isotherms reported by Miskidzh'yan and Trifonov (4) show maxima at about 60 mole % acetic acid. Those reported by Naumova (7) show maxima at about 62 mole % acetic acid although it is stated that the maxima occur at about 67 mole % acetic acid. Where comparison is possible (at 0°C.) there is but poor agreement between the viscosity-composition curves of these workers. Certainly the conclusion reached by Naumova indicating the existence of a compound $\text{HNO}_3 \cdot 2\text{CH}_3\text{COOH}$ does not appear valid. From surface tension and refractive index measurements Miskidzh'yan and Trifonov (5) found only evidence of a 1 : 1 molecular compound between acetic acid and nitric acid. Further evidence that the only interaction between the two acids is along these lines only has been adduced by Chedin and Feneant (2) on the basis of Raman spectra measurements.

The existence of Pictet's diacetylorthonitric acid thus appears unsupported by all available data. Since the discovery by Pictet and Genequand of what was taken as a definite compound— $(\text{CH}_3\text{COO})_2\text{N}(\text{OH})_2$ —was based primarily on the results of a distillation procedure it was decided to investigate the liquid-vapor equilibria for the system nitric acid - acetic acid. The results are of a preliminary nature only but are strongly suggestive of the presence of a maximum boiling azeotrope at about 65 to 70 mole % acetic acid. In order to minimize decomposition the fractionations were carried out at reduced pressures. Two boiling point - composition curves were obtained—one at 100 mm. and the other at 200 mm.—the maximum boiling points being 77° and 95°C. respectively. The general shapes of the curves show an appreciable difference between the liquid and vapor compositions around the azeotropic composition. It is thus possible to explain the observations of Pictet and Genequand regarding the distillations of nitric acid - acetic acid mixtures. The large main fraction will obviously possess the azeotropic composition which corresponds roughly with the formula assigned by them to diacetylorthonitric acid. As confirmation for our view that this so-called "compound" is merely a mixture of the two acids we have determined the "molecular weights" of (1) a 2 : 1 mole mixture of acetic acid and nitric acid respectively and (2) the "diacetylorthonitric acid" prepared according to the distillation method described by Pictet and Genequand. Freezing point depressions in ethylene bromide yield values of approximately 170 for the "molecular weight" in both cases, in

reasonable agreement with a value of 185 recorded for "diacetylorthonitric acid" by Pictet and Genequand. The simple mixture thus appears to be identical with the "compound" obtained on distillation. The high observed "molecular weight" can perhaps be attributed to departure from ideal behavior or to intermolecular association. In acetic acid as a solvent we have obtained cryoscopic molecular weights of from 215 to 240, while Pictet and Genequand report a value of 238 for the "compound". These values are, however, readily explained since if we really have a mixture of 1 mole of nitric acid and 2 moles of acetic acid the calculated molecular weight of *nitric* acid comes out about 70. Furthermore, a rough measurement of the "molecular weight" of the "compound" from the freezing point depression in dioxane gave a value of 66.

Pictet and Genequand report that the specific gravity of "diacetylorthonitric acid" is 1.189 at 23°C. and that its refractive index is 1.3843 (μ_D at 23°C.). Both these constants are suspiciously close to those obtained for a straight 1 : 2 mole mixture of nitric acid and acetic acid—density, 1.187 at 25°C. (7) and refractive index 1.3816 (μ_D at 35°C.) (5).

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DROPPING AMALGAM ELECTRODES¹

BY R. C. TURNER AND C. A. WINKLER

Abstract

The anodic limiting current at a lead amalgam dropping electrode is shown to be proportional to the concentration of the lead in the amalgam, at constant flow rate. The original Ilkovic equation does not apply to the anodic limiting current from dropping amalgam electrodes.

The anodic limiting currents with lead and cadmium amalgams have been found to agree with the 2nd approximation of the Ilkovic equation, as derived by Strehlow and Stackelberg for this process, for flow rates in the region below approximately 1.2 mgm. per sec. With flow rates greater than this, the lead amalgams gave a linear relation between the anodic limiting current divided by concentration and the mass flow rate. With cadmium amalgams no such linear relation was evident and the magnitude of the limiting current depended on the size of the drops as well as on the mass flow rates. The half wave potentials of lead and cadmium were found to depend on the flow rate of the dropping electrode.

Introduction

Strehlow and Stackelberg (6) have shown, both theoretically and experimentally, that the original Ilkovic equation does not apply to the limiting current from the oxidation of metals in an amalgam dropping electrode. They derived, as second approximation of the Ilkovic equation, the following expression for this process:

$$I_{d-} = 607nCD^{1/2} m^{2/3} t^{1/6} (1 - KD^{1/2} m^{-1/3} t^{1/6}) \quad (1)$$

or

$$I_{d-}/Cm^{2/3} t^{1/6} = 607nD^{1/2} - 607nKDm^{-1/3} t^{1/6}, \quad (2)$$

where C is the concentration (millimoles per liter) of metal in the amalgam, I_{d-} is the anodic limiting current (microamperes), D is the diffusion coefficient of the metal in the amalgam (square centimeters per second), m and t are respectively the mass flow rate (milligrams per second) and drop time (seconds per drop) and K is a constant. In the same paper, it was shown that the half wave potential of a metal soluble in mercury is not independent of the mass flow rate and drop time of the dropping electrode.

In a thesis presented at this University by one of the authors (8) in September 1949, results were given which showed, among other things, that the anodic limiting current from the oxidation of the metals in lead, cadmium, and zinc amalgam dropping electrodes is not expressed by the original Ilkovic equation, as had been formerly assumed (2, 3). A calculation was also given to show that the half wave potential from a dropping amalgam could not be strictly constant with changing rates of flow for these metals. This was done by assuming I_{d-}/c equal to k_a in the equation

¹ Manuscript received in original form July 17, 1950, and, as revised January 18, 1951.

Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, with financial assistance from the National Research Council, and the Division of Chemistry, Science Service, Department of Agriculture, Ottawa, Scientific Contribution No. 187, Division of Chemistry, Science Service.

$$E_{1/2} = E^1 + \frac{RT}{nF} \ln \frac{f_s k_a}{f_a k_s}, \quad (3)$$

where $E_{1/2}$ is the half wave potential, E^1 , R , n , T , and F are constants, f_s and f_a are respectively the activity coefficients of ions in solution and metals in the amalgams at the amalgam-cell solution interface, and k_s is equal to $605 nD^{1/2} m^{2/3} t^{1/6}$ (of the Ilkovic equation $I_d = 605 nD^{1/2} m^{2/3} t^{1/6} C$). At the time when the paper by Strehlow and Stackelberg appeared, work was in progress to determine (a) the true relation between the anodic limiting current, mass flow rate, and drop time of a dropping amalgam electrode, and (b) the effect, if any, of the flow rate on the half wave potential of lead and cadmium.

In the present paper are given the results of the investigations that have been made in this laboratory. The amalgams used were 6 to 45 times more dilute than the cadmium amalgam used by Strehlow and Stackelberg (6) and the range of flow rates was greater. In general, the results are in agreement with their conclusions.

Experimental

For part of the work, the polarographic equipment was essentially of the standard manually operated type (3). There was, however, a small glass cup, supported by a handle attached to the stopper of the cell, under the end of the dropping electrode. This served to prevent the amalgam from falling into the quiet pool of mercury and allowed the amalgam to be removed to determine

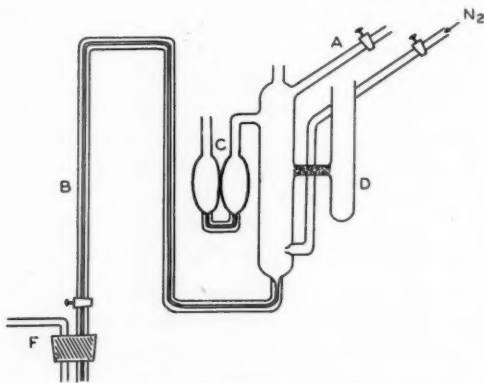


FIG. 1. Polarographic cell.

its weight. During the investigation, the cell shown in Fig. 1 was introduced for operational convenience. The capillary of the dropping electrode (0.05 mm. bore) passed through the hole in the top of the cell and was sealed in place with de Khotinsky cement. The cell could be supplied with electrolyte through *A* without dismantling the apparatus. Amalgam could be removed to determine its weight, or the cell completely emptied, through the capillary

B by suction supplied to an Erlenmeyer flask attached to *F*. The quiet electrode *D*, which was a saturated calomel electrode, was attached to the cell through an asbestos packed tube. A trap, *C*, allowed escape of the purified nitrogen (9) which was bubbled through the solution to remove oxygen. The cell, except the straight part of capillary *B* to which *F* was attached was suspended in a constant temperature water bath which was maintained at $25 \pm 0.02^\circ\text{C}$.

Amalgams were prepared in an Erlenmeyer flask; the flask had a short piece of glass tubing sealed to the bottom, and one end of the electrode capillary was sealed into the tubing with de Khotinsky cement. The flask was swept with nitrogen or carbon dioxide prior to dissolving the metal in the mercury. The mass flow rate of the amalgam was controlled with nitrogen or carbon dioxide pressure.

The indifferent electrolyte was 0.1 *M* potassium chloride and the maximum suppressor used was methyl violet in the early work which was later replaced with 0.01% gelatine. Dilute amalgams were generally used as the dropping electrodes but a few experiments were made using mercury. All currents were corrected for residual current.

During the investigation into the effect of mass flow rate on the half wave potential, the potential of the quiet electrode was checked, at the beginning and at intervals during each experiment, against a second saturated calomel electrode. The potential of the dropping electrode was calculated from the external potential applied, with reference to the saturated calomel electrode used for checking the working half cell. Correction was applied for the *IR* drop of the cell and the circuit resistance in series with the cell. Half wave

potentials were determined from plots of $\log \frac{I - I_{d-}}{I_{d+} - I}$ versus *E* (7), where *I*

is the current corresponding to a given potential *E*, and *I*_{d+} is the cathodic diffusion current, with the convention that *I*_{d-} is negative and *I*_{d+} is positive.

Results and Discussion

During the early work, a beaker was used as the electrolytic cell and the mass flow rate was determined immediately after an experiment was made. Fig. 2 shows the proportionality obtained between the anodic limiting current and lead concentration when this concentration was varied from 0 to 0.89 millimolar. The effect of variation in flow rate on the anodic limiting currents for lead, cadmium, and zinc amalgams are shown respectively in Tables I, II, and III. In all cases the quantity $I_{d-}/Cm^{2/3} t^{1/6}$ varied directly with flow rate while with lead and cadmium the ratio $I_{d+}/Cm^{2/3} t^{1/6}$ was relatively constant. When sufficient methyl violet was added to the cell solution to prevent a maximum in the anodic current from the zinc amalgam, it was found that the cathodic current was practically nonexistent regardless of the zinc concentration in solution. The results in Table III were therefore obtained without the addition of zinc ions to the solution.

It was found that changing the concentration of lead acetate in solution from 0 to 2.5 millimolar had an insignificant effect on the anodic limiting current, with a lead amalgam of 0.82 millimolar concentration. It was concluded that the anodic limiting current was not affected by the rate at which metal ions diffused away from the drop.

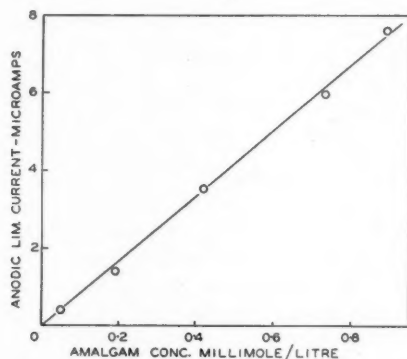


FIG. 2. Effect of concentration of lead amalgam on the anodic limiting current.

TABLE I

EFFECT OF FLOW RATE OF LEAD AMALGAM ON THE LIMITING CURRENTS

Amalgam concentration: 0.69 millimolar.

Electrolyte: 0.1 *M* potassium chloride, 0.002 *M* hydrochloric acid, 0.50 millimolar lead acetate, trace of methyl violet

Drop time, sec./drop	Flow rate, mgm./sec.	$m\frac{1}{2} t^{\frac{1}{2}}$	$I_{d+}/m\frac{1}{2} t^{\frac{1}{2}}$ *	$I_{d-}/m\frac{1}{2} t^{\frac{1}{2}}$
3	2.49	2.21	2.31	3.33
4	1.93	1.95	2.28	3.05
5	1.59	1.78	2.30	2.89
6	1.29	1.60	2.31	2.59

* Subsequent analysis of the lead acetate salt used in this experiment showed that it contained more lead than was indicated by the formula on the reagent bottle.

TABLE II

EFFECT OF FLOW RATE OF CADMIUM AMALGAM ON THE LIMITING CURRENTS

Amalgam concentration: 1.20 millimolar.

Electrolyte: as in Table I, except 1.00 millimolar cadmium chloride instead of lead acetate

Drop time, sec./drop	Flow rate, mgm./sec.	$m\frac{1}{2} t^{\frac{1}{2}}$	$I_{d+}/m\frac{1}{2} t^{\frac{1}{2}}$	$I_{d-}/m\frac{1}{2} t^{\frac{1}{2}}$
3	2.62	2.28	3.71	7.57
4	2.14	2.09	3.57	6.00
5	1.67	1.84	3.66	5.82
6	1.40	1.69	3.73	5.75

TABLE III

EFFECT OF FLOW RATE OF ZINC AMALGAM ON THE ANODIC LIMITING CURRENT
 Amalgam concentration: 2.08 millimolar.
 Electrolyte: 0.1 *M* potassium chloride, 0.002 *M* hydrochloric acid, methyl violet.

Drop time, sec./drop	Flow rate, mgm./sec.	$m^{\frac{1}{3}} t^{\frac{1}{6}}$	$I_d - / m^{\frac{1}{3}} t^{\frac{1}{6}}$
3	2.51	2.22	10.95
4	1.85	1.90	10.32
5	1.56	1.69	9.88
6	1.20	1.52	9.67
7	1.05	1.43	9.09

In the subsequent work the cell shown in Fig. 1 was used, carbon dioxide replaced nitrogen over the amalgams, and gelatine was used in place of methyl violet. The mass flow rates were determined while the limiting currents were flowing. The lead amalgams varied from 0.30 to 1.37 millimolar and the cadmium amalgams were 0.47 and 0.54 millimolar. Cadmium chloride, 0.54 millimolar, or lead nitrate, 0.50 millimolar, was added to the cell solution when the presence of cadmium or lead ions was desired. By using three different capillaries, mass flow rates varying from 0.07 to 6.66 mgm. per second were obtained.

(a) *Relation Between Flow Rate of Dropping Amalgam Electrodes and Anodic Limiting Currents*

The lower section of Fig. 3 shows that a plot of the anodic limiting current divided by the concentration of lead in the amalgams against mass flow rate gave a linear relation over a range of flow rates from about 0.5 to 4.4 mgm. per sec., regardless of the size of the drops. On the other hand, with the cadmium amalgam (upper section of Fig. 3) this linear relation does not exist, even for a given drop size. The magnitude of the limiting current apparently depends on both the size of the drops and the mass flow rate. With both metals, however, the curves in Fig. 3 are similar in the region below mass flow rates of 0.5 mgm. per sec., in that they both bend sharply toward zero current for zero flow rate. The curves calculated from Equation (1) (the values for *D* and *K* are explained later) agree reasonably well with the experimental results up to mass flow rates of roughly 1.2 mgm. per sec.

The results taken from Fig. 3 were plotted to conform to the treatment used by Strehlow and Stackelberg (6), that is, $I_d - / Cm^{2/3} t^{1/6}$ is plotted against $t^{1/6} / m^{1/3}$. According to Equation (2), this should yield a straight line with slope $-607 nkD$ and intercept on the $I_d - / Cm^{2/3} t^{1/6}$ axis equal to $607 nD^{1/2}$. Sufficient results were available for only 8.70 mgm. drops with cadmium amalgams and 9.35 mgm. drops with lead amalgams to indicate a definite trend. A few results for very slow flow rates with lead amalgams of drop weights between 6.00 and 7.00 mgm. are also shown. In the lower section of Fig. 4 the straight line is that found experimentally by Strehlow and Stackelberg for cadmium amalgam with *K* equal to 28.5. It apparently fits the

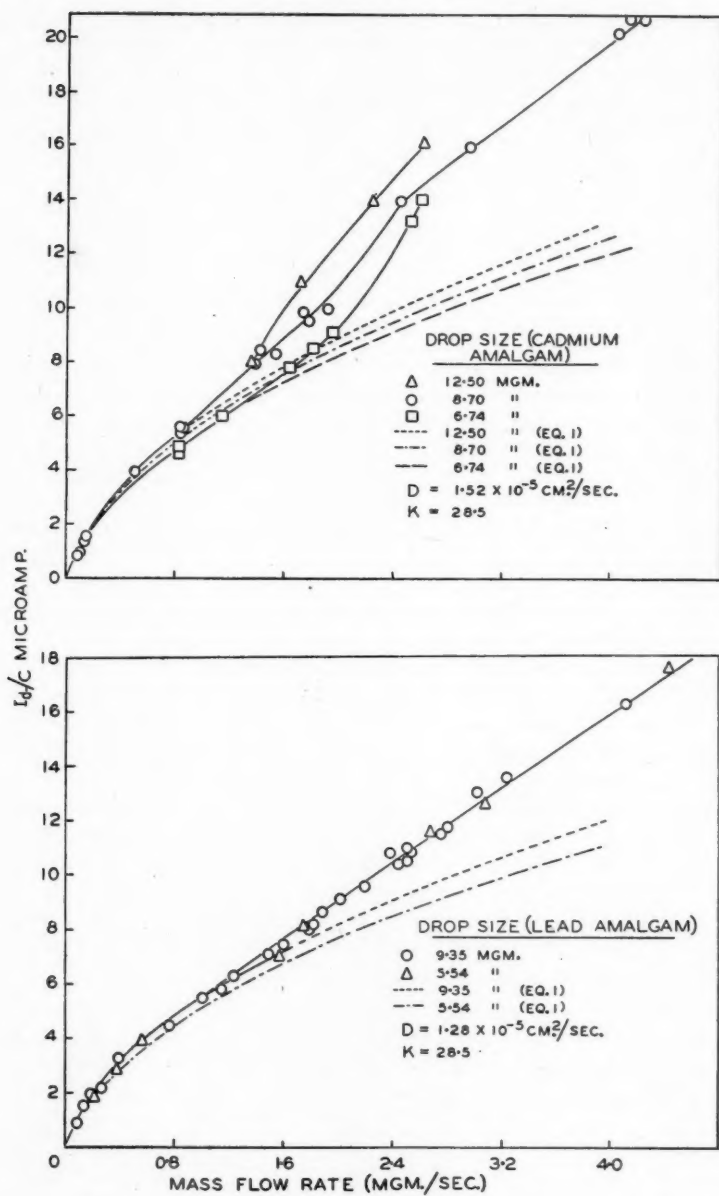


FIG. 3. Effect of flow rate of amalgam on the anodic limiting current.

present results for values of $t^{1/6}/m^{1/3}$ from 1.4 to 5.2. For values of $t^{1/6}/m^{1/3}$ below 1.2 the experimental values deviate from the line rather abruptly, supposedly because of the rinse effect (6). In the upper section of Fig. 4, which shows the same plot for lead amalgams, the straight line was drawn through the experimental points with a slope and intercept given by Equation

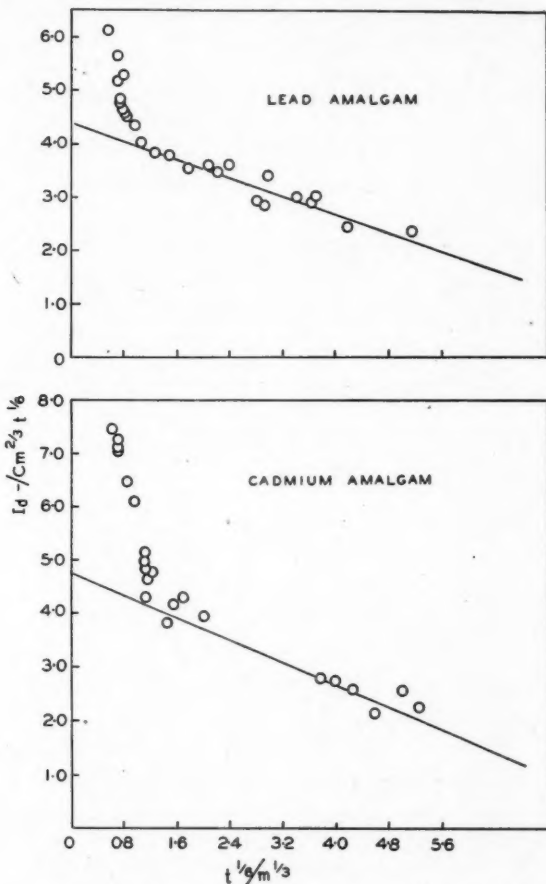


FIG. 4. $I_d - C_m^{2/3} t^{1/6}$ versus $t^{1/6}/m^{1/3}$ plot for amalgams.

(2) (K equal to 28.5). The diffusion coefficient for cadmium in mercury, calculated from the straight line in the lower section of Fig. 4, is 1.52×10^{-5} cm². per sec. (6) and for lead the diffusion coefficient, calculated in the same way from the upper section of Fig. 4, is 1.28×10^{-5} cm². per sec. Admittedly, slightly different straight lines could be drawn in Fig. 4, which would fit the experimental results and Equation (2), and thus correspond to somewhat differ-

ent diffusion coefficients. However, the fact that the calculated diffusion coefficients are of the right order of magnitude (1, 10) increases confidence in Equation (1).

Some of the average anodic limiting currents with flow rates less than 0.2 mgm. per sec. were calculated from the area under current-time curves for individual drops. This procedure gave essentially the same results as the usual method with a damped galvanometer.

(b) *Effect of Flow Rate on the Half Wave Potential of Lead and Cadmium*

The $\log \frac{I - I_d - I}{I_d + I}$ versus E plots were straight lines for both lead and cadmium (Fig. 5) with reciprocal slopes of -0.032 . This is in general agree-

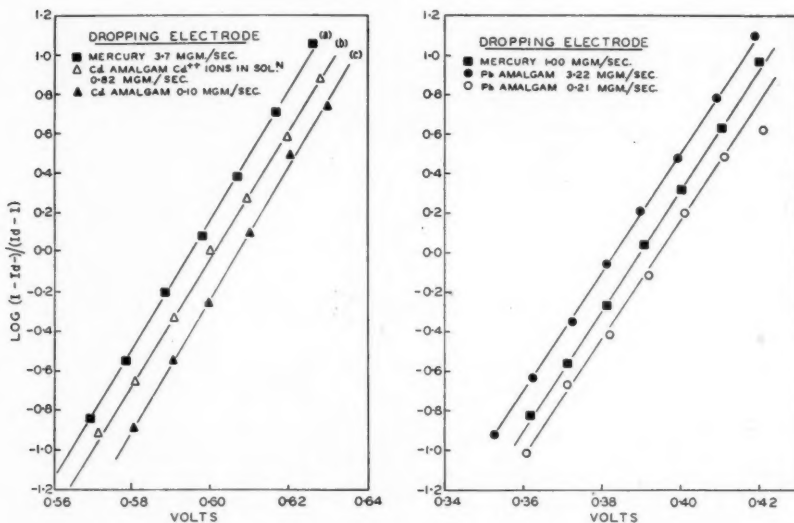


FIG. 5. Current-potential relation.

ment with the results reported for dropping amalgam electrodes (5) and also conforms to the theoretical reciprocal slope of -0.03 for 25°C . Apparently, from the left section of Fig. 5, the type of electrode reaction taking place had no effect on the shape or slope of the curves, since Curve (a) was entirely reduction of ions, Curve (b) was entirely oxidation of metal atoms, and Curve (c) was both oxidation and reduction.

The effect of mass flow rate of the dropping electrode on the half wave potential is summarized in Fig. 6. The results were similar for the two metals, that is, an increase of flow rate was accompanied by a less negative half wave potential. This agrees with the results of Strehlow and Stackelberg (6) for

the reduction of cadmium and tellurium ions. At very slow flow rates the half wave potentials were much more negative than for flow rates generally used in polarography. Possibly convection currents in the cell solution became an important factor at the very fast flow rates (4).

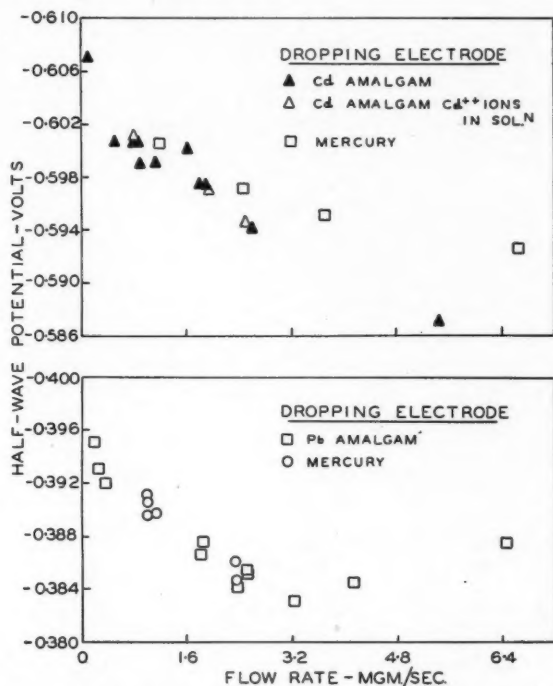


FIG. 6. Effect of flow rate of the dropping electrode on half wave potentials.

Acknowledgment

Grateful acknowledgment is made to the Committee on Research, McGill University, for financial assistance in the preparation of this manuscript.

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PREPARATION OF N-SUBSTITUTED UREAS FROM NITROSOMETHYLUREAS¹

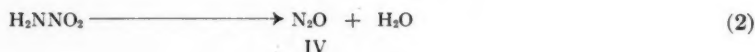
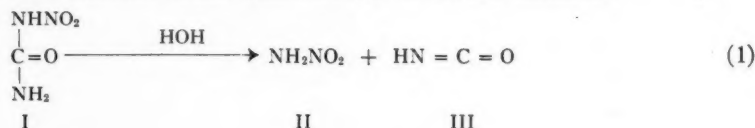
BY JEAN L. BOIVIN² AND PAUL A. BOIVIN³

Abstract

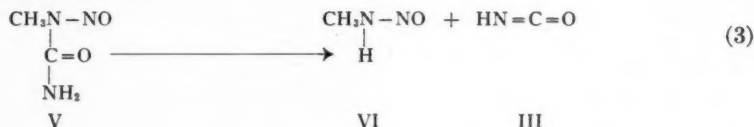
Good yields of N-substituted ureas were obtained by reacting amines with N-nitroso-N-methylurea in aqueous solution. It has been shown that N-nitroso-N-methylurea decomposed into methylnitrosamide and isocyanic acid. Similarly, N-nitroso-N, N'-dimethylurea and amines gave rise to good yields of N-substituted-N'-methylureas.

Introduction

Davis and Blanchard (4) have shown that nitrourea (I) decomposed in aqueous solution into isocyanic acid (III) and nitramide (II) which is transformed into nitrous oxide (IV) and water. The formation of isocyanic acid was inferred from the reaction of nitrourea in aqueous solution with amines to yield N-substituted ureas, quantitatively in several instances.



The reaction of nitrosoureas with amines has not been studied. However, it may be postulated that N-methyl-N-nitrosourea (V) decomposes in aqueous solution into N-methyl-N-nitrosamide (VI) and isocyanic acid (III) according to the mechanism suggested by T. L. Davis (Equations (1) and (2)). In strongly alkaline solution compound V is known to yield diazomethane. When N-methyl-N-nitrosourea (V) was boiled in aqueous solution, the stoichiometric amount of nitrogen was evolved and the solution was found to contain isocyanic acid and methanol. With amines, as was expected, the isocyanic acid produced yielded N-substituted ureas (VII) according to the following equation:-



¹ Manuscript received January 8, 1951.

Contribution from the Organic Section of the Canadian Armament Research and Development Establishment, Valcartier, Quebec, and the Chemical Laboratories of University of Ottawa, Ottawa, Ont.

² Defence Research Board, Valcartier, Quebec.

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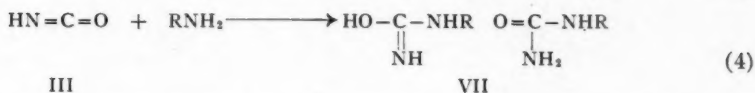


Table I shows some of the substituted ureas prepared, together with their physical properties and yields. Nearly quantitative yields were obtained and in several cases purification was unnecessary.

TABLE I
N-SUBSTITUTED UREAS¹, RNHCONH₂ (VII)

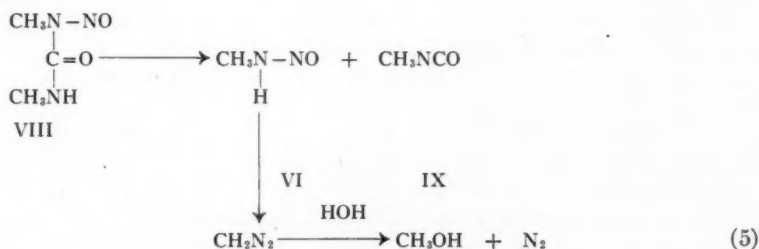
N-Substituent R	Reaction time, min.	Yield, %	M.p. °C.		Solvents	Ref.
			Observed	Recorded		
Methyl	5	96.1	101	102	Ethanol plus ether	4
Ethyl	5	92.1	92	92-92.4	Ethanol plus ether	4
<i>n</i> -Propyl	5	86.8	107	107	Ethanol plus ether	3
<i>n</i> -Butyl	5	85.8	96	96	Ethanol plus ether	4
<i>n</i> -Amyl	3	70.8	75 ²	75	Water	5
<i>n</i> -Hexyl	5	88.6	109.5	109.5	Water	7
Cyclohexyl	12	86.8	195-196	195-196	Water	11
Phenyl	20	91.0	146-147	147	Water	4
Benzyl	15	80.0	147-147.5	147-147.5	Water	13
Amino	1	100	227-234d	214-235d	Ethanol	10
Anilino	5	100	172	171-172	Ethanol	8
<i>p</i> -Tolyl	20	85.3	181-182	181-182	Ethanol	12
<i>p</i> -Chlorophenyl	30	90.4	212d	212d	Ethanol	15
Diethyl	1	91.9	75	75-75.3	Ether	4

¹ All melting points are uncorrected.

² Isolated as the nitrate.

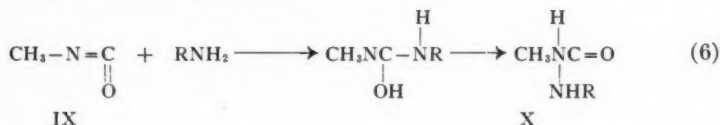
³ Semicarbazide isolated as its benzal derivative.

In addition to this series of N-substituted ureas, other derivatives of ureas were made from N, N'-dimethyl-N-nitrosourea (VIII). This starting material has been found to decompose in aqueous solution according to the following scheme:-



When compound VIII was boiled with water, nitrogen was evolved quantitatively in accordance with Equation (5), and methyl isocyanate (IX) was formed as was shown by its hydrolysis to methylamine and carbon dioxide. Similarly to N-nitroso-N-methylurea, the reaction of amines with N-nitroso-N, N'-dimethylurea proceeded through the formation of methyl nitrosoamide

(VI) and methyl isocyanate (IX), the latter reacting with amines to yield N-methyl-N'-substituted ureas (X).



The yields were excellent and, in most cases, the N-substituted-N'-methylureas did not require further purification. The results are given in Table II.

TABLE II
N-SUBSTITUTED-N'-METHYLUREAS, RNHCONHCH₃ (X)

N-Substituent R	Reaction time, min.	Yield, %	M.p. °C.		Solvents	Ref.
			Observed	Recorded		
Methyl	12	73.8	100	100	Ether	6
Ethyl	3	88.0	52-53	52-53	Ether	14
<i>n</i> -Propyl ¹	5	84.3	67-68		Ether	
<i>n</i> -Amyl ²	2	94.3	75-76		Diluted ethanol	
Cyclohexyl ³	3	90.4	157-158		Diluted ethanol	
Phenyl	12	77.7	150.5-151.5	150.5-151.5	Diluted ethanol	6
Benzyl	4	84.2	98-99	98-99	Diluted ethanol	9
Anilino	20	76.0	154-155	154-155	Water	6
Amino	2	92.1	114-115	112-118	Ethanol plus ether	2
<i>p</i> -Tolyl	10	87.1	178	178	Ethanol	1
<i>p</i> -Chlorophenyl	10	88.7	200	200	Diluted ethanol	1

¹Calc. for C₈H₁₃ON₂: N, 24.1%. Found: N, 23.8%.

²Calc. for C₇H₁₆ON₂: N, 19.4%. Found: N, 19.3%.

³Calc. for C₈H₁₆ON₂: N, 17.9%. Found: N, 17.2%.

Experimental

Effect of Boiling Water on N-methyl-N-nitrosoarea

In a flask equipped to measure the gas evolved was placed N-methyl-N-nitrosoarea (3.8450 gm.; 0.0414 mole) and water (125 ml.). The mixture was boiled and the solid dissolved with evolution of gas. The volume of gas which was collected over a solution of sodium hydroxide (20%) was found to be 808 ml. (calc. 816 ml.). The presence of isocyanic acid was shown in the following way: A slight excess of silver nitrate was added to the solution and a white precipitate soluble in ammonia and nitric acid was formed. However, the amount of isocyanic acid produced was not quantitative.

The presence of methyl alcohol was shown by the oxidation of a portion of the solution with potassium dichromate in strong sulphuric acid. After distilling a portion of this solution, the distillate contained formaldehyde as was shown by the derivative obtained with 2, 4-dinitrophenylhydrazine, m.p. 166-167°C.

Effect of Boiling Water on N-Nitroso-N, N'-dimethylurea

Using the procedure described above, N-nitroso-N, N'-dimethylurea (2.6920 gm.) was boiled with water. Nitrogen evolved: 542 ml. (calc. 552 ml.). No precipitation took place with a silver nitrate solution, indicating the absence of isocyanic acid. The formation and identification of methylamine and carbon dioxide indicated the transient formation of methyl isocyanate. The presence of methyl alcohol was demonstrated as described above.

Preparation of N-substituted ureas (VII)

N-Methyl-N-nitroso-urea (0.1 mole) was reacted with an amine (0.1 mole) in aqueous solution (200 ml.). The solution was boiled until the evolution of gas ceased. Then it was evaporated under reduced pressure and the residue recrystallized from a suitable solvent. Results are listed in Table I. In several cases, recrystallization did not change the melting point of the product.

Preparation of N-Substituted-N, N'-dimethylurea (X) from N, N'-Dimethyl-N-nitroso-urea (VIII)

The procedure used for the preparation of these substances was the same as the one described above for the preparation of N-substituted ureas (VII). The results are listed in Table II.

Acknowledgment

The authors express their thanks to the Defence Research Board of Canada for permission to publish this paper.

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6-IODOMETAMECONINE AND 3-IODOMETAHMIPINIC ACID¹

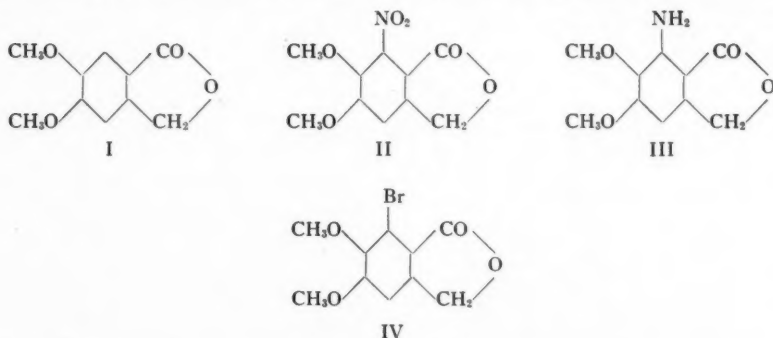
By J. A. McRAE, R. B. VANORDER, F. H. GRIFFITHS, AND
THELMA ESKIN HABGOOD

Abstract

6-Iodo-*m*-meconine has been prepared from *m*-meconine by several steps and oxidized to 3-iodo-*m*-hemipinic acid. The orientation of the iodo-*m*-meconine is based on its conversion to 4, 5, 6-trimethoxyphthalide. The identity reported by Rây and Robinson of the bromo-*m*-meconine made directly by similar steps from *m*-meconine with that from 2-bromoveratric acid and formaldehyde could not be confirmed. The former substance has the orientation ascribed to it by Rây and Robinson but the identity and orientation of the latter substance is left in doubt. Attempts to form a substituted diphenyl ether from dimethyl 3-iodo-*m*-hemipinate and the potassium salt of methyl vanillate failed.

Some years ago we became interested in the halogenated metameconines as possible intermediates in the synthesis of 2, 3, 2'-trimethoxydiphenyl ether-5, 6, 4'-tricarboxylic acid which it was thought might be a degradation product of the alkaloid cularine (12). Our efforts to make this substance have so far failed but the substituted metameconines themselves proved to be of considerable interest and we now report on our work on some of these.

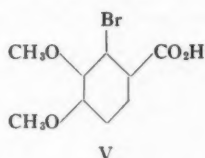
Owing to the work of Edwards, Perkin, and Stoye (3) and that of Rây and Robinson (16) *m*-meconine (I) is now a relatively easily accessible substance.



Rây and Robinson stated also that *m*-meconine could be easily nitrated in the 6-position to give II and that this nitro compound could be reduced to the amine (III) which in turn could be transformed through a diazo reaction into 6-bromo-*m*-meconine (IV), melting point 223°C. This same bromo-*m*-meconine, according to these authors, could be produced also by the action of formaldehyde on 2-bromoveratric acid (V), a method of synthesis which seemed to leave no doubt as to the structure of the 6-bromo-*m*-meconine made from

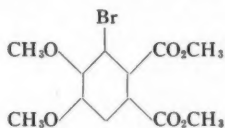
¹ Manuscript received November 6, 1950.

Contribution from the Department of Chemistry, Queen's University, Kingston, Ontario.

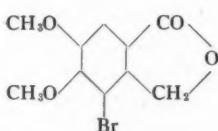


m-meconine, and thus establishing as well the orientation of compounds (II) and (III). When their work was repeated nitro-*m*-meconine and amino-*m*-meconine were found to have the melting points ascribed to them by Rây and Robinson but the 6-bromo-*m*-meconine produced from amino-*m*-meconine melted at 207°C. More significantly this bromo-*m*-meconine was found not to be identical with the substance made from 2-bromoveratric acid which had indeed a melting point of 223°C. A mixed melting point determination made on these two substances showed a large depression; these observations have been repeatedly verified by ourselves and other workers in these laboratories. The proof of the orientation of the substance IV offered by Rây and Robinson was clearly inadequate.

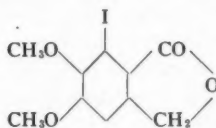
The orientation advanced by Rây and Robinson for 6-nitro-*m*-meconine (IV) and for the corresponding amino and bromo compounds is nevertheless correct. When the bromo-*m*-meconine, melting point 207°C. made from amino-*m*-meconine was oxidized, and the acid produced esterified by means of diazomethane, dimethyl 3-bromo-*m*-hemipinate (VI) was obtained identical in properties with the authentic ester described by Faltis and Frauendorfer



VI

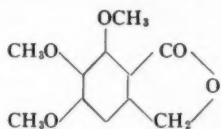


VII

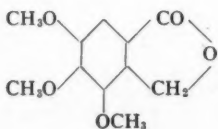


VIII

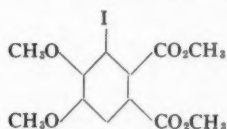
(4). The bromo-*m*-meconine was therefore either 6-bromo-*m*-meconine (IV) or 3-bromo-*m*-meconine (VII). When diazotized amino-*m*-meconine was treated with potassium iodide an iodo-*m*-meconine (VIII) was obtained. This on treatment with potassium methylate gave the new substance 4, 5, 6-trimethoxyphthalide (IX). The structure of this phthalide was obvious since it proved to be not identical with the known 3, 4, 5-trimethoxyphthalide (X)



IX



X



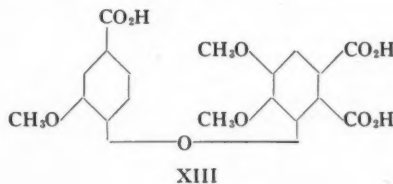
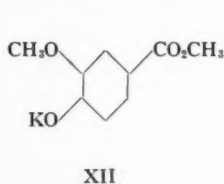
XI

made from gallic acid by Alimchandani and Meldrum (1) and by King and King (11) and therefore structure (IX) was the only other possibility for the substance made from this iodo-*m*-meconine. In this way the orientation of substances (II), (III), and (IV) was verified.

The reactions just mentioned provide a convenient route to certain substituted *m*-meconines and the corresponding *m*-hemipinic acids, otherwise difficult to obtain. Faltis and Frauendorfer (4) prepared 3-bromo-*m*-hemipinic acid by a lengthy synthesis from papaverine; Manske, Ledingham, and Holmes were unable to obtain 4, 5, 6-trimethoxyphthalide (IX) from 2, 3, 4-trimethoxybenzoic acid with either formaldehyde or chloral. We have been unable to synthesize phthalides bearing an iodo or nitro group by the action of formaldehyde on iodo- or nitro-veratric acids respectively. In contrast 3-iodo-*m*-hemipinic acid was readily prepared by the oxidation of 6-iodo-*m*-meconine (VIII) and characterized as its dimethyl ester (XI).

The structure of the substance of melting point 223°C. derived in very small yield from 2-bromoveratric acid and formaldehyde is still under investigation.

Dimethyl 3-bromo-*m*-hemipinate and 3-iodo-*m*-hemipinate were applied in an attempted synthesis of 2, 3, 2'-trimethoxydiphenyl ether-5,6,4'-tricarboxylic acid (see formula XIII). Faltis, Holzinger, Ita, and Schwarz (5) pointed out that the formation of diphenyl ether-carboxylic esters from metallic phenolates and halogenated methoxybenzoic esters becomes rapidly more difficult as the number of groups ortho to the proposed ether linkage increases. This difficulty has been verified by Manske (12) and ourselves. No reaction occurred when dimethyl 3-bromo-*m*-hemipinate (VI) was heated under a variety of conditions with the potassium salt of methyl vanillate (XII) in the presence of copper powder. When the more reactive dimethyl 3-iodo-*m*-hemipinate was used in place of the bromo ester the expected ether (XIII) was not produced. Instead veratric acid was the only substance isolated, the dimethyl 6-iodo-*m*-hemipinate acting as a methylating agent. This interesting example of methylation was observed by us in 1939 prior to the description of similar instances by King (9) and King and Wright (10). The latter authors have discussed the subject fully. Following the example of Faltis, Holzinger, Ita, and Schwarz (5) we sought to avoid this undesired reaction by reacting 6-iodo-*m*-meconine with potassium methyl vanillate, hoping thereby to form a substance which could be oxidized to the desired tricarboxylic acid. Although a reaction occurred a pure product was not isolated. Experiments with these reactants are being continued.



Experimental

meta-Meconine

Some changes were made in the method of Rây and Robinson (16). Veratric acid was made from vanillin by methylation (2) and oxidation (3). Then veratric acid (50 gm.), glacial acetic acid (250 ml.), concentrated hydrochloric acid (200 gm.), and a solution of formaldehyde (40%, 60 ml.) were heated together with stirring under reflux at 90–95°C. for 10 hr. and then at 100°C. for a further three hours. The crude material was sometimes isolated by the method of Rây and Robinson in yields of 55–65%; recrystallization from glacial acetic acid gave a pure product of melting point 155°C. At other times the reaction mixture was diluted with water (500 ml.), cooled with stirring, and filtered from some deposited tars. The filtrate was then evaporated almost to dryness, the residue taken up in boiling water (1500 ml.), again filtered from a fragrant tar, and the filtrate cooled. Fawn-colored needles, melting point 154–156°C*, were recovered in a yield of 33%.

6-Nitro-m-meconine

The method here described was found to give greater yields than the method of Rây and Robinson (16). A cold mixture of concentrated sulphuric acid (10 ml.) and concentrated nitric acid (40 ml.) was mechanically stirred and cooled in an ice bath while *m*-meconine (28 gm.) was added over a period of one hour. After the addition was complete, more concentrated nitric acid (100 ml.) was added, the mixture stirred for four hours, and treated with ice (300 gm.). The yellow precipitate was recovered, washed repeatedly with water, and then with boiling alcohol (100 ml.). When crude *m*-meconine isolated by the method of Rây and Robinson was used for nitration, the yield of the crude 6-nitro-*m*-meconine was only 48–56%, but when the purer *m*-meconine obtained by the alternative method described above was nitrated, the yield of crude 6-nitro-*m*-meconine was 71%, and its melting point was 178.5–179.5°C. Repeated recrystallization of the product from ethanol and from glacial acetic acid raised its melting point to 182.0–182.5°C.; Rây and Robinson reported 183–184°C.

6-Amino-m-meconine

The nitro compound was converted to the hydrochloride of 6-amino-*m*-meconine by the method of Rây and Robinson (16) in yields of 75%. Conversion of the salt to the free amine followed by recrystallization of the amine from dilute alcohol gave 6-amino-*m*-meconine of melting point 159.5–160.5°C.; Rây and Robinson reported 158°C.

6-Bromo-m-meconine

Recrystallized 6-amino-*m*-meconine (8 gm.) was treated with water (120 ml.) and hydrobromic acid (16 ml. of density 1.585) and the mixture mechanically stirred and cooled to –5°C. while a solution of sodium nitrite (3.4 gm.) in

* All melting points are corrected.

water (20 ml.) was slowly added. Diazotization occurred very slowly; stirring and cooling were continued for 160 min. after the addition was complete, and then the excess nitrous acid was destroyed with urea. The solution was then added to a cold solution of cuprous bromide (made from 10 gm. of copper sulphate pentahydrate) in hydrobromic acid (15 ml. of density 1.585), the mixture was heated for a few minutes on the steam bath, cooled, and the product recovered in 74% yield. Repeated recrystallizations from butanol with charcoal and from mixtures of ethanol and acetic acid gave colorless needles in a yield of 3.7 gm. or 35%, melting point 207–207.5°C. Calc. for $C_{10}H_9O_4Br$: Br, 29.26%. Found: Br, 29.48%. The same substance was also made by following the directions of Rây and Robinson who used hydrochloric acid instead of hydrobromic acid in the diazotization.

Oxidation of 6-Bromo-m-meconine

6-Bromo-*m*-meconine (3 gm.) was oxidized with alkaline permanganate in the usual way, and the resulting 3-bromo-*m*-hemipinic acid after being recrystallized from water melted at 174.5°C. Faltis and Frauendorfer (4) reported a melting point of 175–176°C. Calc. for $C_{10}H_9O_6Br$: equivalent weight, 153; Found: equivalent weight, 155.

The acid was converted into its dimethyl ester in yields of 95% by means of diazomethane; after recrystallization from methanol, the dimethyl ester of 3-bromo-*m*-hemipinic acid so obtained had a melting point of 88°C., while Faltis and Frauendorfer reported 87–88.5°C.

Reaction of 2-Bromoveratric Acid and Formaldehyde

2-Bromoveratric acid was made either from 2-aminoveratric acid (14) by the method of Rây and Robinson (16) or by the method of Raiford and Perry (15); the same product of melting point 205°C. was obtained by both routes. In each of numerous trials, 2-bromoveratric acid (4 gm.) was heated with formaldehyde, hydrochloric acid, and acetic acid, as described by Rây and Robinson. After being repeatedly recrystallized, the product had a melting point of 223°C. as reported by these authors, but when the product was mixed with the 6-bromo-*m*-meconine of melting point 207°C. obtained from 6-amino-*m*-meconine, the melting point fell to 180–193°C.

6-Iodo-m-meconine

6-Amino-*m*-meconine hydrochloride (5.9 gm.) was diazotized with sodium nitrite and hydrochloric acid. After the excess nitrous acid had been destroyed, a solution of potassium iodide (6 gm.) in water (15 ml.) was added and after the reaction the free iodine was removed with sodium bisulphite. The orange precipitate that separated in 72% yield was collected and recrystallized repeatedly from glacial acetic acid with charcoal to give pale yellow needles of 6-iodo-*m*-meconine, melting point 169–170°C. Calc. for $C_{10}H_9O_4I$: I, 39.69%. Found: I, 39.40%.

3-Iodo-m-hemipinic Acid

When 6-iodo-*m*-meconine (11 gm.) was oxidized at 50–60°C. with alkaline permanganate, and the acid product repeatedly recrystallized from water, 3-iodo-*m*-hemipinic acid was obtained in a yield of 70%, melting point 177.5°C. Calc. for $C_{10}H_9O_6I$: equivalent weight, 176; I: 36.08%. Found: equivalent weight, 179; I, 35.82%.

Dimethyl Ester of 3-Iodo-m-meconine

The foregoing acid was converted with almost quantitative yield into the dimethyl ester by means of diazomethane. Recrystallized from methanol the ester had a melting point of 81.5°C. Calc. for $C_{12}H_{13}O_6I$: I, 33.42%. Found: I, 33.30%.

4, 5, 6-Trimethoxyphthalide

Potassium (0.8 gm.) was dissolved in thoroughly dried methanol (50 ml.), mixed with 6-iodo-*m*-meconine (3.2 gm.) and copper bronze (Kahlbaum's No. 02219, 0.1 gm.), and heated under reflux for 12 hr. The copper bronze was then removed and the filtrate diluted and acidified. The product that separated (1.7 gm.) was repeatedly recrystallized from water with charcoal to give colorless needles of melting point 136.5–137°C. Calc. for $C_{11}H_{12}O_6$: C, 59.0; H, 5.35; OCH_3 , 41.5%. Found: C, 58.7, 58.8; H, 5.29, 5.25; OCH_3 , 39.36%.

Samples of 3,4,5-trimethoxyphthalide were made by Dr. Manske and by one of us (J.A.M.) respectively, according to the directions of King and King (11) and found to melt at 135°C. as described. Mixed melting point determinations made with each of these samples and 4,5,6-trimethoxyphthalide melted indefinitely at 111–114°C. Both the 4,5,6-trimethoxyphthalide and 3,4,5-trimethoxyphthalide on oxidation produced phthalic acids which melted at 173–173.5°C. with frothing, and a mixed melting point of the two acids showed no depression. The proof of identity was inconclusive because of the dependence of the so-called melting points upon the rate of heating. According to Alimchandani and Meldrum (1), 3,4,5-trimethoxyphthalic acid has a melting point of 176–177°C.

Attempts to produce 4,5,6-trimethoxyphthalide from 6-bromo-*m*-meconine did not succeed.

Attempts to Synthesize 2,3,2'-Trimethoxydiphenyl Ether-5,6,4'-Tricarboxylic Acid

Vanillic acid (Schuchardt) was converted into methyl vanillate in the usual way. Efforts to bring about ether formation between this phenolic ester and methyl 3-iodo-*m*-hemipinate were made in three ways.

Following the procedure for diphenyl ether formation used by Faltis and Frauendorfer (4), potassium (0.4 gm.) was dissolved in absolute methanol (15 ml.) and added to methyl vanillate (4.5 gm.), the last-named chemical

being in considerable excess. A solution of dimethyl 3-iodo-*m*-hemipinate (3.8 gm.) in methanol (10 ml.) was added and the mixture evaporated to dryness under reduced pressure. The dry material was mixed with copper bronze (British Drug Houses, 0.07 gm.) and copper acetate (0.04 gm.) and heated in an oil bath for one hour at 154°C. and then for two hours at 165°C. On cooling, the mixture was extracted thoroughly with ether and the ethereal solution shaken with 2*N* sodium hydroxide solution and dried over sodium sulphate. Evaporation of the ether left an oil which solidified. This was recrystallized from methanol when 1 gm. of material was obtained. It was hydrolyzed by methanolic potassium hydroxide and on acidification veratric acid was obtained, since its melting point of 178°C. was not depressed by admixture with authentic veratric acid, and since its methyl ester had the same melting point (58°C.) as that reported for methyl veratrate. No other pure compounds could be isolated. When methyl vanillate was used in amounts equivalent to the potassium methylete, similar results were obtained.

The second variation was according to the modification used by Faltis and Zwerina (6). Potassium methylete was prepared by adding potassium (0.7 gm.) to absolute methanol (10 ml.). To this was added methyl vanillate (3.5 gm.) and the whole evaporated to dryness under reduced pressure with slight warming. The dry potassium salt of the ester was mixed as rapidly as possible with a mixture of dimethyl 3-iodo-*m*-hemipinate (6 gm.), Kahlbaum's copper bronze (Natur kupfer C) (0.1 gm.), and cupric acetate (0.1 gm.); the whole was heated in an oil bath at 150–170°C. for three hours. Only veratric acid could be isolated from the reaction mixture.

The third essay was based upon the procedure used by Harington and Barger (7) in the synthesis of thyroxine. Dimethyl iodo-*m*-hemipinate (1.5 gm.) was heated under reflux for 24 hr. with methyl vanillate (1 gm.), anhydrous potassium carbonate (2 gm.), copper bronze (0.05 gm.), and copper acetate (0.03 gm.) in anhydrous dioxane (30 ml.) No iodide ions were produced, showing that the conditions used were too mild. Even when potassium methylete and methanol were used in place of potassium carbonate and dioxane respectively no action occurred, and the use of triethylene glycol at 170°C. as the solvent in place of methanol did not bring about the reaction in six hours.

6-Iodo-m-meconine and Methyl Vanillate

A mixture of potassium (0.6 gm.) dissolved in absolute methanol (15 ml.), methyl vanillate (4.5 gm.), and 6-iodo-*m*-meconine (3.2 gm.) was evaporated to dryness under reduced pressure. Copper bronze (0.07 gm.) was mixed with the dry residue and the mixture heated for one hour at 155°C. and for two hours at 165°C. There was ample evidence that reaction had occurred, but prolonged attempts did not lead to the isolation of any pure products. Further trials will be made with this general method.

Acknowledgments

Thanks are due to Dr. R. Y. Moir, Dr. Norah McGinnis (Mrs. W. Glen), and to H. M. Collins for assistance with some of the experimental work, and to Dr. R. H. Manske for discussions of the problem and for a specimen of 3, 4, 5-trimethoxyphthalide. We are grateful to Canadian Industries Ltd. for the award of a fellowship which enabled one of us (T.E.H.) to participate in this work.

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HYDROGEN PEROXIDE AND ITS ANALOGUES

III. ABSORPTION SPECTRUM OF HYDROGEN AND DEUTERIUM PEROXIDES IN THE NEAR ULTRAVIOLET¹

BY M. K. PHIBBS AND PAUL A. GIGUÈRE

Abstract

The absorption of ultraviolet light between 3000 and 4000 Å by solutions of hydrogen peroxide in water and of deuterium peroxide in heavy water has been measured at various concentrations. Both peroxides show slight but real deviations from Beer's law at high concentrations. Substitution of hydrogen by deuterium shifts the absorption continuum by about 390 cm.⁻¹ towards shorter wave lengths. This shift is of the same order as that calculated from the difference in zero-point energy of the two isotopic molecules.

A number of investigators (1, 3, 5, 9, 10, 11, 12, 15) have shown that hydrogen peroxide absorbs very strongly in the ultraviolet, beginning in the neighborhood of 4000 Å and increasing rapidly without any sign of reaching a maximum, at least as far as 2000 Å. Most of the measurements were made on dilute solutions, however. Recently Taylor and Cross (14) measured the absorption of concentrated solutions, 50% and 90%. As part of a research program on the properties of deuterium peroxide a small amount of this compound was prepared by passing an electric discharge through the vapor of heavy water. It was felt of interest to study its absorption in the near ultraviolet in order to compare it with that of ordinary hydrogen peroxide.

Experimental

The measurements were made with a Beckman DU spectrometer using a pair of matched quartz cells 10 mm. thick. In all cases the absorption of the solutions was compared with that of the pure solvent. Even under ultraviolet illumination the peroxide solutions were quite stable so that interference from gas bubbles was negligible. The hydrogen peroxide solutions were prepared by diluting a 99.3% solution obtained by vacuum distillation of Becco's 90% commercial product. It was observed that the solutions were much more stable when a dilute peroxide solution rather than redistilled water was used as diluent. The method of production of deuterium peroxide will be fully described in a subsequent paper. A 6.5% and a 30.7% solution of the isotopic compound in heavy water essentially free of ordinary hydrogen were available for this investigation.

Discussion of Results

In Table I are listed the values of a , the absorption coefficient in Beer's law, $\log I/I_0 = -a c d$, where the concentration c is in moles of peroxide per

¹ Manuscript received February 20, 1951.

Contribution from the Department of Chemistry, Laval University, Québec, Que., with financial assistance from the National Research Council of Canada.

TABLE I

ABSORPTION COEFFICIENTS OF HYDROGEN AND DEUTERIUM PEROXIDES IN THE NEAR ULTRA-VIOLET

Wave length in Å	Wt % H ₂ O ₂ in H ₂ O			Wt % D ₂ O ₂ in D ₂ O	
	6.5	54.9	99.3	6.5	30.7
3050	1.55			1.12	
3100	1.12			0.794	
3200	0.550			0.398	0.331
3300	0.251	0.178		0.186	0.170
3400	0.117	0.0977	0.0776	0.0852	0.0795
3500	0.0537	0.0457	0.0389	0.0427	0.0372
3600	0.0256	0.0209	0.0182	0.0195	0.0170
3700	0.0112	0.0102	0.00871		0.0085
3800	0.00661	0.00540	0.00437		0.00428
3900	0.00399	0.00302	0.00224		0.0019
4000		0.00208	0.00120		
4100			0.000562		
4200			0.000257		
4300			0.000141		

liter of solution and d , the thickness of the absorbing layer in cm. The plot of $\log a$ at various wave lengths (Fig. 1) fits closely a straight line for each concentration; this is not surprising as the range covered is limited and seemingly far from any absorption maximum. A slight parabolic curvature becomes apparent when the plot is extended to 2000 Å using the data of previous workers. The results of Taylor and Cross agree quite well with the present

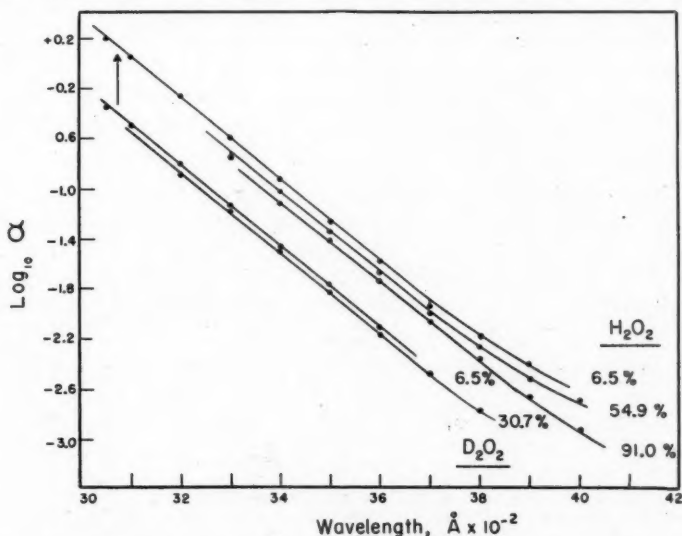
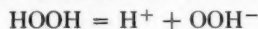


FIG. 1. Absorption coefficient of hydrogen and deuterium peroxides at various concentrations. The curves for deuterium peroxide have been shifted down by 0.4 unit of the ordinate scale to avoid confusion.

ones except at longer wave lengths, where they show a certain dip away from straight lines. The fact that these authors used the photographic method may account for the small difference. At any rate they were the first to report the deviation from Beer's law which the present results substantiate. They suggested the repression of ionization in concentrated solutions



as responsible for part of the decrease in absorption. Indeed, Bredig and his coworkers (3) have shown that addition of sodium hydroxide to hydrogen peroxide enhances markedly the ultraviolet absorption of the latter. Their data and interpretation would indicate that the absorption coefficient of the OOH^- ion is about ten times greater than that of the neutral molecule. However, this cannot account for more than a fraction of the noted deviation since pure hydrogen peroxide is very slightly ionized, in fact hardly more so than water. Rather it is likely that the deviation is due to molecular association in the liquid state; both water and hydrogen peroxide form strong hydrogen bonds and there is little doubt that the potential energy curves of molecules are modified by their environments. As far as can be judged from the data in Table I, solutions of deuterium peroxide deviate from Beer's law to the same extent as those of hydrogen peroxide.

The other noticeable result of this investigation is the shift towards shorter wave lengths of the absorption continuum of deuterium peroxide with respect to that of hydrogen peroxide. Such isotope shifts, at least on the long wave length side of the absorption curve, are exhibited by other molecules involving excitation to an upper repulsive energy level. In the case of water this effect amounts to $900\text{--}1200\text{ cm.}^{-1}$ (6); the present results for 6.5% solutions indicate an average shift of 390 cm.^{-1} for the peroxides. As it is unlikely that isotopic substitution can alter significantly the potential energy surfaces the main effect must be due to difference in zero-point vibrational energy between the two molecules.

Now the various fundamental frequencies of both peroxides are known with fair accuracy so that an approximate calculation of the isotope shift is possible. The data in Table II are based on recently measured infrared and Raman spectra of the two compounds in the liquid state (4, 7, 13). The zero-point energy difference in the ground state, given by the difference in the half sum

TABLE II
FUNDAMENTAL VIBRATIONS OF HYDROGEN AND DEUTERIUM PEROXIDES*

Mode	H ₂ O ₂	D ₂ O ₂
ν_1	3410 cm.^{-1}	2530 cm.^{-1}
ν_2	1400	1030
ν_3	880	880
ν_4	660	540
ν_5	3430	2500
ν_6	1350	1010

* Rounded-off figures.

of these frequencies, is therefore 1320 cm^{-1} . From this quantity must be subtracted the zero-point energy difference between the two OH and the two OD radicals formed by dissociation. For the present purpose this difference was taken as 940 cm^{-1} , the average between the values for the ground state and the first electronically excited state (8). Indeed, energy considerations (15) indicate that absorption of ultraviolet light by a peroxide molecule must produce one normal and one excited radical,



The calculated shift is therefore $1320 - 940 = 380 \text{ cm}^{-1}$, as compared with the observed one, 390 cm^{-1} .

The agreement is certainly better than could be expected in view of the oversimplifications made. One needs only mention here the case of such simple molecules as the hydrogen halides (2) where the observed shift in the ultraviolet spectrum of the deuterated molecules is about three times that calculated from the zero-point vibrational energies. Differences in the ground-state eigenfunctions and in the form of energy curves have been assumed to account for these facts. The absence of any structure in the spectrum of hydrogen and deuterium peroxides precludes further interpretation of the above results at present.

Acknowledgment

The authors are grateful to the National Research Council for financial and other assistance. The 90% hydrogen peroxide was kindly supplied by the Buffalo Electro-Chemical Co. The deuterium peroxide was prepared in this laboratory by Mr. R. S. Eaton.

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Résumé

L'absorption de la lumière ultra-violette par des solutions de peroxyde d'hydrogène dans l'eau et de peroxyde de deutérium dans l'eau lourde a été mesurée à différentes concentrations dans la région s'étendant de 3000 à 4000 Å. Pour les deux composés l'absorption ne suit pas rigoureusement la loi de Beer surtout aux concentrations élevées. La substitution de l'hydrogène par le deutérium déplace le seuil d'absorption du peroxyde d'environ 390 cm^{-1} vers l'ultra-violet. Cet effet est dû surtout à la différence d'énergie au point zéro des deux molécules isotopiques.

THE DIELECTRIC CONSTANT OF DISULPHUR DECAFLUORIDE¹BY N. R. S. HOLLIES² AND R. L. MCINTOSH³

Abstract

A method is described for obtaining the dielectric constant and conductivity of disulphur decafluoride in both liquid and gaseous forms. The freezing point of the liquid and the molecular weight of the vapor are established as criteria of purity. All the measurements lead to the conclusion that disulphur decafluoride is nonpolar. Its molar polarizations in the two forms are compared with those of other members of the sulphur fluoride and carbon fluoride homologous series as well as with hexane, benzene, and toluene.

Introduction

From the reported properties of disulphur decafluoride (S_2F_{10}) it is difficult to classify the liquid as nonpolar or polar. The reported values of Trouton's constant, 23.3 (18) and 23.0 (6), would seem to indicate that disulphur decafluoride is normal in behavior. The temperature independent parachor, 246.5 (18), is also typical of a nonassociated compound. In the absence of any data on the sulphur fluoride homologous series of which disulphur decafluoride is the second member, the high density, 2.09 at 0°C. (18), and high boiling point, 29°C. (6), could be interpreted as indicating that this fluoride is associated. In addition, all the reported vapor pressure equations for disulphur decafluoride (6, 18) yield an entropy of vaporization of 28.2 or greater. This value is calculated at a vapor concentration of 0.005 moles per liter and when compared with the tabulated values of Hildebrand (17) places disulphur decafluoride in a class between polar and nonpolar compounds.

In this investigation of the dielectric properties of carefully purified samples of disulphur decafluoride it was found that neither liquid nor gaseous phases exhibited any dipole moment, tending to confirm the nonassociated physical structure of the compound (4, 29, 31, 34). The magnitude and the slight temperature dependence of the specific conductivity, 1.94×10^{-10} mho per cm., supports this interpretation (11). The molar polarization of 33.4 cc. places disulphur decafluoride among that group of nonpolar compounds which exhibit a normal "field" volume (8). Hence the electric properties indicate that disulphur decafluoride is a nonpolar, nonassociated, sulphur fluoride.

Dielectric Theory

The determination of dipole moments involves the measurement of dielectric constants. Both the theory of such measurement (4, 10, 36) and the devices used (3, 30, 36) are treated thoroughly elsewhere.

¹ Manuscript received December 8, 1950.

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The polarization of a gas and of some liquids (15, 9) may be calculated by means of the Clausius-Mosotti equation

$$\frac{\epsilon - 1}{\epsilon + 2} \frac{M}{\rho} = 4/3\pi N \left(a_0 + \frac{\mu^2}{3kT} \right) = P_T = (P_E + P_A) + P_0, \quad (I)$$

where ϵ = dielectric constant, M = molecular weight, ρ = density, N = Avogadro's number, a_0 = polarizability, μ = dipole moment, k = Boltzmann's constant, T = absolute temperature, P_T = molar polarization, P_E = electronic polarization, P_A = atomic polarization, P_0 = orientation polarization.

The Clausius-Mosotti expression introduces considerable error when applied to polar liquids. Onsager (28) developed a corresponding equation which allows for interdipole action. Kirkwood (20) has generalized Onsager's theory and arrived at the equation

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{9\epsilon} \frac{M}{\rho} = 4/3\pi N \left(a_0 + \frac{\mu'^2 g}{3kT} \right) = P_T = (P_E + P_A) + P_0, \quad (II)$$

where μ' for the liquid is slightly larger than the moment in the gaseous state and g is a parameter whose value differing from unity is a measure of the hindering of a molecule by its neighbor. Often the gaseous moment can be evaluated quite accurately from further relations developed by Onsager and Kirkwood (28, 20).

*Physical and Chemical Properties of Disulphur Decafluoride**

Disulphur decafluoride was first identified by Denbigh and Whytlaw-Gray (6). They found it to be a colorless volatile liquid of b.p. $29 \pm 1^\circ\text{C}$., m.p. $-92 \pm 1^\circ\text{C}$., density 2.08 ± 0.03 gm. per cc. at 0°C ., surface tension $13.7 \pm 3\%$ dynes per cm., Trouton's constant 23.0, parachor 236, and with the equation for its vapor pressure as a function of temperature, $\log p = -1530/T + 7.95$. More recently a freezing point of -55°C . and a vapor pressure equation $\log p = 2190/T + 24.015 - 6.0 \log T$ have been reported. Experience in handling disulphur decafluoride has shown that the vapor pressure and particularly the freezing point are quite sensitive to impurities, and these facts aid considerably in the recognition of the purity of the compound.

Impurities expected in the disulphur decafluoride samples used in this work were sulphur hexafluoride (SF_6) (24), sulphur monofluoride (S_2F_2) (2), and sulphur tetrafluoride (SF_4) (7) as well as oxyfluorides like thionyl fluoride (SOF_2) (27), and sulphuryl fluoride (SO_2F_2) (37). Silicon tetrafluoride (SiF_4) and carbon tetrafluoride (CF_4) are also formed in the presence of glass and rubber in the reaction system.

A practical separation of disulphur decafluoride from these products depends for the most part on the fact that it is inert to alkali (5), a property shared only by sulphur hexafluoride (24), carbon tetrafluoride (39), and

*Extreme care should be exercised in handling disulphur decafluoride because of its toxicity.

sulphuryl fluoride (26). Hence an alkaline wash serves to remove all but these three impurities from disulphur decafluoride samples (7, 14, 25, 26, 32). In addition, according to the vapor pressure equation of Yost and Claussen (42), silicon hexafluoride has a vapor pressure of 2665 cm. at 0°C. compared with 23.5 cm. of disulphur decafluoride. In contrast sulphuryl fluoride has a vapor pressure of 24.1 cm. at -80°C. (26) and the vapor pressure of carbon tetrafluoride at -128°C. is 76 cm. (14). Hence simple fractionation should be sufficient to remove these remaining impurities in disulphur decafluoride samples. In actual experience the purification process had to be refined further. To remove adhering traces of still another sulphur fluoride the samples were very carefully fractionated. This new product has not been identified but appears to have a higher molecular weight than disulphur decafluoride.

Experimental

(a) Purification

Crude disulphur decafluoride was passed through a scrubbing train of 10% sodium hydroxide into a conventional vacuum manifold where it was stored in 100 cc. bulbs surrounded by liquid air. Sulphur hexafluoride was removed from these by slow fractionation from one bulb at 0°C. to another at -78°C. and the excess volatile component pumped off through a charcoal trap. For final treatment all dielectric samples were fractionated in a 60 cm. column constructed on the design of Bowen and Cooke (1). In order to obtain reliable freezing points of the various disulphur decafluoride fractions and to establish these freezing points as criteria of purity the cell depicted in Fig. 1 was used.

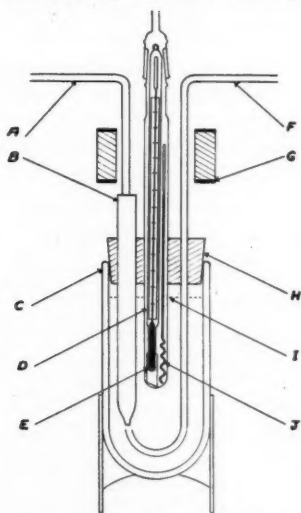


FIG. 1. Freezing point cell.

- A — Liquid air inlet; B — copper reservoir; C — Dewar flask;
D — sample level; E — pentane thermometer; F — compressed air inlet;
G — stirrer solenoid; H — insulating cork; I — acetone level;
J — magnetic stirrer.

When attached directly to the vacuum manifold a sample could be condensed in the inner bulb and its freezing point determined. The pentane thermometer in the inner bulb, a German standard, which could be read to 0.1°C ., was checked at the Dry Ice - acetone and mercury points where the error in its reading was less than 0.1°C . so its values were used directly in all experimental results. The cooling rates were easily controlled and plots of time vs. temperature revealed long flat regions when the cooling was very slow. The temperatures of these regions corresponded to the first appearance of crystals in the bulb and were taken as the true freezing points of the samples under investigation.

The other main criterion of purity was sought in molecular weight determinations of the various fractions used. These were determined by the well known vapor density method. The molecular weights were plotted against pressure and the value obtained by extrapolation to zero pressure was taken as the true experimental molecular weight.

(b) Dielectric Measurements

Capacity measurements for dielectric work are made in various ways. Perhaps the most versatile of these come under the classification of "Bridge Methods" (13, 16, 33). These possess some advantage over other methods in that condenser leakage can be measured directly and determinations can be carried to quite low frequencies. The Schering circuit used in this investigation is shown in Fig. 2. Both the detector and oscillator employ some special techniques which bear consideration.

In order to obtain sufficiently accurate measurements on gaseous disulphur decafluoride, the filter network also shown in Fig. 2 was added (a parallel resonant filter tuned to 3440 c.p.s.). Detection was carried out using two Sylvania oscilloscopes in series in a manner similar to that adopted by Lamson (21).

The R-C oscillator of Fig. 3 in conjunction with a voltage regulated power supply acted as the power source. The design of the driver circuit was that suggested by Dr. Watson (38) based on those described by Ginzton and Hollingsworth (12). The highly stable output (120 v., 8 w.), negligible frequency drift (over the range of 400 to 6000 c.p.s.), and low harmonic content of the output (less than 1%) make the oscillator particularly useful in such bridge applications where the power source ratings and characteristics are quite exacting. With these generator and detector circuits it was possible to maintain the consistency of the Schering bridge at one part in seventy thousand.

(c) Dielectric Cells

The cell used for dielectric measurements on liquid disulphur decafluoride is shown in Fig. 4. The brass condenser cylinders were insulated from one another by small Lucite rings at each end, and four holes drilled in the outer shell gave the liquid sample access to the interior. A supply of ethylene glycol was circulated through the copper cooling coil surrounding the cell.

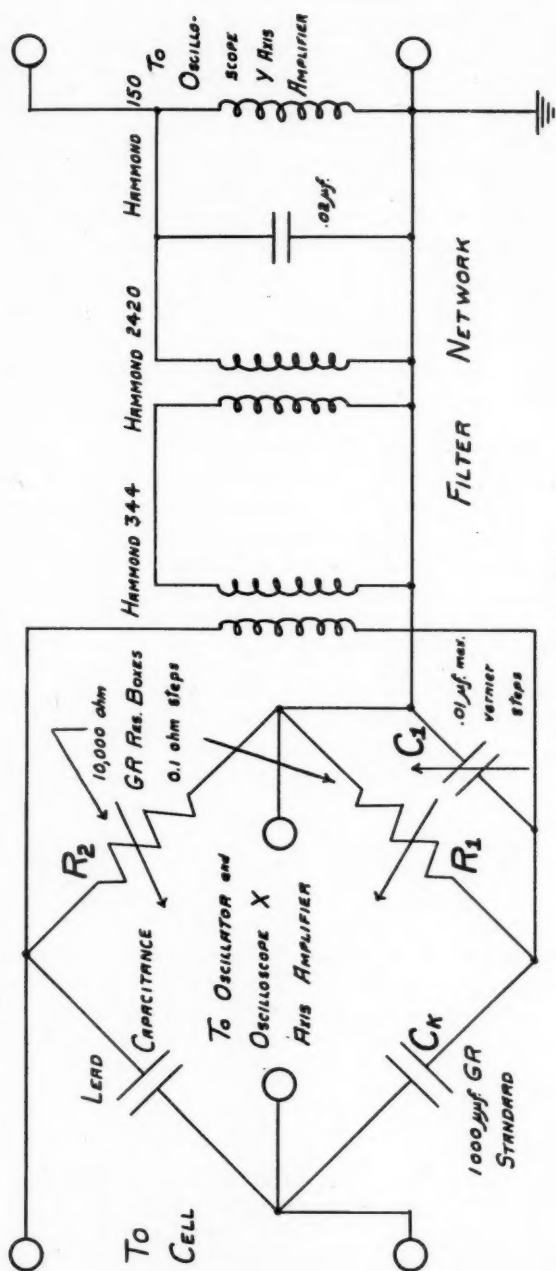


FIG. 2. Schering bridge.

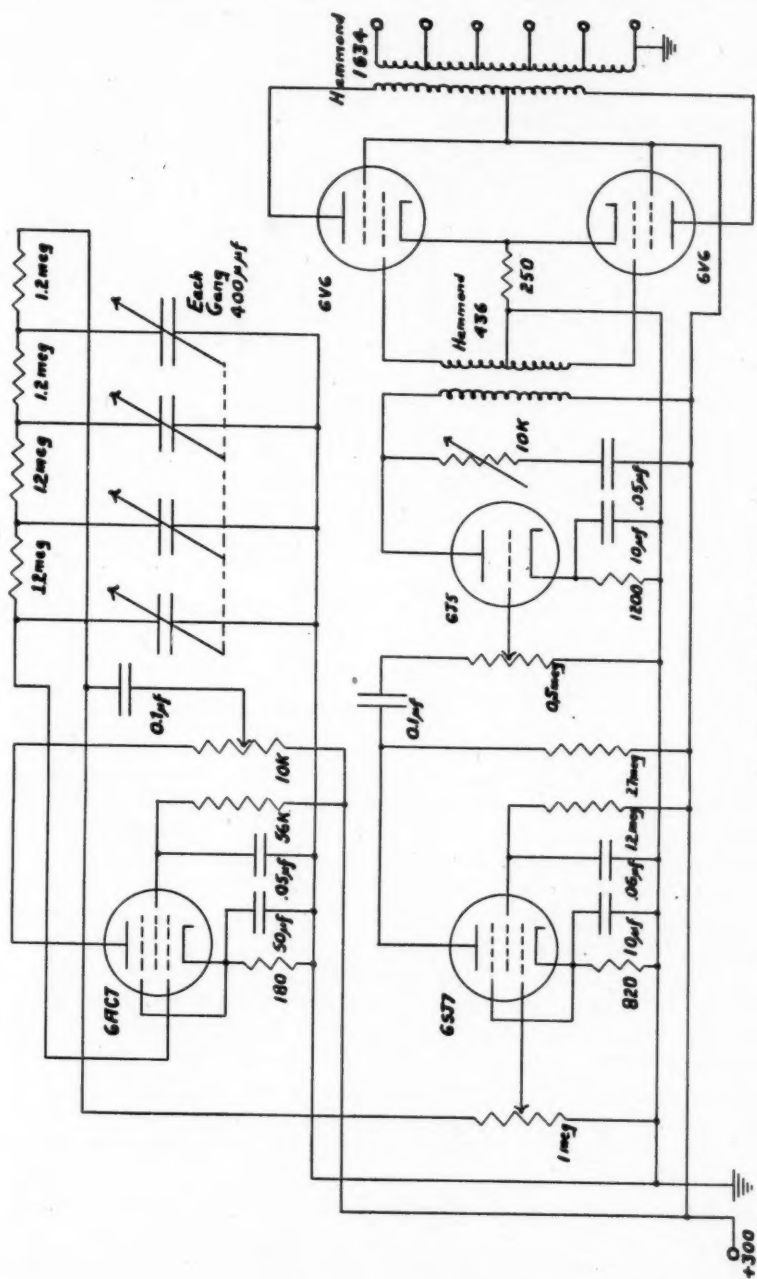


FIG. 3. Phase shift oscillator.

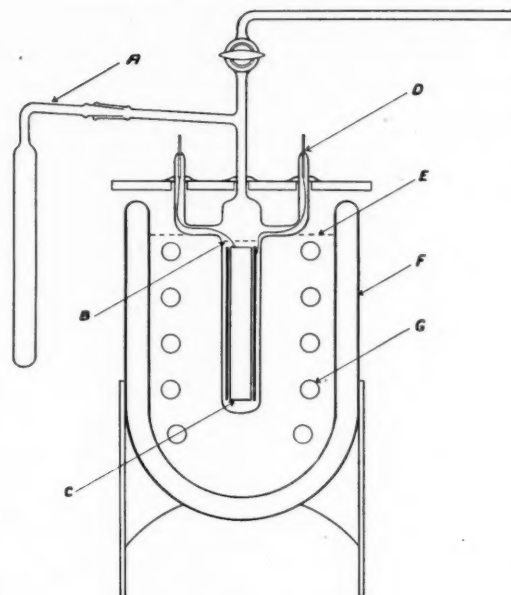


FIG. 4. Dielectric cell for liquids.

A — Filling bulb; B — sample level; C — cell condenser;
 D — metal-to-glass seal for lead; E — glycol level;
 F — Dewar flask; G — cooling coil.

This supply originated in a four gallon storage tank which could be cooled by a commercial refrigerator or warmed with electric heaters. With such a temperature controlling scheme it was possible to maintain the cell within $0.002^{\circ}\text{C}.$ of any temperature from -30 to $+60^{\circ}\text{C}.$ for periods up to several hours. The temperature was followed in all runs by a pentane thermometer immersed in the Dewar next to the cell. Filling was accomplished by means of the side arm and bulb attached to the top of the cell. Samples were condensed by liquid air into the bulb and on warming were poured into the cell proper by simple rotation about the ground glass joint. The cell was shielded by grounding the metal holder, copper cooling coil, and metal framework which held it in place. The $200\ \mu\text{mf.}$ capacity of the cell showed complete stability with time which was interpreted as revealing that both the brass and Lucite were not attacked by disulphur decafluoride.

The cell used with gaseous disulphur decafluoride was constructed along very similar lines but with a higher evacuated capacity of $1360\ \mu\text{mf.}$ designed to match the optimum sensitivity range of the Schering circuit used. It consisted of two concentric brass cylinders $25\ \text{cm.}$ long, $4\ \text{cm.}$ in diameter with $0.003\ \text{in.}$ clearance, again separated by Lucite rings and the cell drilled to give the vapor easy access to the interspace. The cylinders were mounted hori-

zontally in a Pyrex bulb and connected to the bridge leads through widely spaced side arms and Pyrex-tungsten seals. In this case ample electric shielding was provided by grounding the metal frame of the 25°C. water bath surrounding the cell. Any desired vapor pressure of disulphur decafluoride could be maintained in the cell by connecting it directly with the freezing point cell in which the temperature of the liquid phase could be controlled. The equilibrium pressure was easily read from the U-tube manometer which was left connected to the manifold during any gaseous dielectric run. Again, capacity stability of this cell at 25°C. even over long periods of evacuation not only indicated inertness of the cell materials to disulphur decafluoride but also revealed that there was negligible sorption of disulphur decafluoride by the insulating rings.

Results

(a) Importance of Purity

Preliminary runs on the various liquid disulphur decafluoride fractions revealed evidence of the type depicted in Table I. The molecular weights given were determined at 235 mm. pressure and the dielectric constants at 10°C.

TABLE I
ANALYSIS OF FRACTIONATION 13

Fraction		1st	2nd	3rd
Molecular weights	Before dielectric runs	255	259	257
	After dielectric runs	255	259	256
		255	258	257
Freezing points	Before dielectric runs	-54.2	-55.5	-55.3
	After dielectric runs	-55.0	-55.8	-55.4
Dielectric constant		2.029	2.031	2.032

These results indicated clearly that in the relatively pure state, molecular weights of disulphur decafluoride varied little from fraction to fraction, whereas the freezing points were highly sensitive not only to fractionation but to a large extent to handling and storage of the various samples. Hence the freezing points of best fractions could be used as a delicate test of the purity of the sample. Allied with this, such figures also showed that the measured dielectric constant was affected very slightly by the impurities, increasing the significance of any dielectric figures obtained on fairly pure samples. This is borne out in the comparison of the more detailed dielectric studies on fractions 13-3 and 15-2.

(b) Variation of the Dielectric Constant with Temperature

Table II shows the observed dielectric data of two purified samples of disulphur decafluoride as a function of temperature. Lead capacity cor-

TABLE II
LIQUID DIELECTRIC CELL CAPACITIES AS A FUNCTION OF TEMPERATURE

Sample no.	F.p., °C.	T, °C.	C, $\mu\text{mf.}$	C _{evac.} 0°C. $\mu\text{mf.}$	$\frac{dC_{\text{evac.}}}{dT}$ $\mu\text{mf./}^\circ\text{C.} \times 10^3$
13-3	-55.4	21.9	402.3	239.8	11
		20.0	403.1		
		17.6	404.1		
		14.7	405.3		
		12.0	406.5		
		8.8	407.6		
		5.7	409.0		
		2.4	410.2		
		-1.2	411.6		
		-4.7	413.0		
15-2	-54.2	20.50	405.79	243.05	9.3
		12.90	409.00		
		6.65	411.64		
		1.40	414.76		
		-3.05	415.58		
		-8.05	417.58		
		-11.30	418.88		

rections have already been made. The figures given for fraction 15-2 were obtained using all the bridge refinements developed for measurements on gases.

Plots of these values gave smooth curves which were interpolated at the temperatures of Table III. Dielectric constants were evaluated using the evacuated cell constants of Table II. Molar polarizations were calculated from Equations (I) and (II) in order to compare the Clausius-Mosotti approach with that of Kirkwood and Onsager. These along with liquid densities of disulphur decafluoride, determined by Hugill (18), are recorded in Table III.

As a check on the purity of fraction 15-2 a portion of the sample was analyzed by the vapor density procedure, and the molecular weight curve of Fig. 5, obtained. The intercept at zero pressure, 253.5, lies within experimental error of the theoretical value, 254.1, and is used in all the polarization calculations on this sample.

TABLE III
MOLAR POLARIZATIONS OF LIQUID DISULPHUR DECAFLUORIDE

Sample No.	Temp., °C.	Dielectric constant	Density, gm./cc.	Polarization, cc.	
				C-M	K-O
13-3	-4.0	2.071	2.107	31.74	35.65
	4.0	2.054	2.081	31.75	35.58
	12.0	2.037	2.054	31.77	35.50
	20.0	2.020	2.028	31.78	35.42
15-2	-10.0	2.0847	2.1270	31.69	35.62
	0.0	2.0638	2.0936	31.70	35.55
	10.0	2.0423	2.0607	31.72	35.46
	20.0	2.0202	2.0274	31.74	35.58

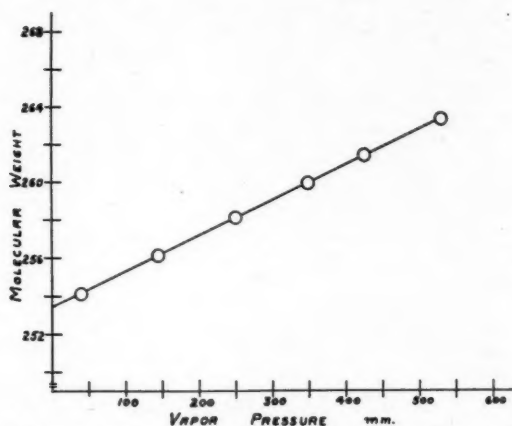


FIG. 5. Molecular weight as a function of pressure for disulphur decafluoride fraction 15-2.

The a-c. conductivity of these samples can be calculated from the resistive loss figures obtained at every bridge balance point. From the geometry of the cell and these values the specific conductivity at 3440 c.p.s. and 0°C. is 1.94×10^{-10} mho per cm. It exhibits a very small temperature coefficient.

(c) *Dielectric Constant of Gaseous Disulphur Decafluoride*

As a check on the results obtained with liquid disulphur decafluoride, measurements were made on the purified gas at 25.0°C. as a function of pressure. Data for a typical run can be seen in Table IV.

These values are plotted in Fig. 6. Again it was deemed legitimate to interpolate capacity values at intervening pressures and in particular for those pressures for which the vapor densities were known (Fig. 5.). These values, along with the empty cell capacity (1402.88 $\mu\mu\text{f.}$), were corrected for lead error (42.52 $\mu\mu\text{f.}$) and the dielectric constant as a function of pressure evaluated as in Table V. In conjunction with the determined molecular weight of

TABLE IV
GASEOUS DIELECTRIC CELL CAPACITY AS A FUNCTION OF PRESSURE USING FRACTION No. 15-2, f.p. -54.2°C.

Pressure, mm.	Capacity, $\mu\mu\text{f.}$
9.6	1403.02
48.8	1403.26
115.6	1403.74
171.3	1404.14
219.0	1404.50
292.2	1405.04
351.8	1405.50
406.2	1405.92
475.0	1406.46
518.7	1406.78

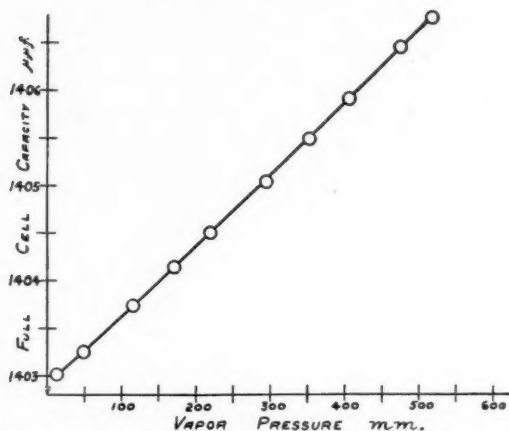


FIG. 6. Gaseous dielectric cell capacity as a function of pressure using fraction 15-2.

TABLE V
DIELECTRIC CONSTANT OF SAMPLE NO. 15-2 (GASEOUS)

Pressure, mm.	Density, gm./cc.	Dielectric constant	Molar polarization, cc.
39.4	0.0005352	1.00023	36
144.2	0.0019698	1.00078	33.5
249.0	0.0034334	1.00136	33.5
349.0	0.0048387	1.00191	33.3
426.0	0.0059406	1.00234	33.3
532.2	0.0074765	1.00295	33.3

sample No. 15-2 and the Clausius-Mosotti equation, the ϵ values were used to compute the molar polarizations of the table.

We have an alternative way of obtaining the true gaseous molar polarization value if we assume that the vapor is ideal and use ideal densities (8). Taking the equation

$$P_T = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{\rho}$$

$$\text{then using } \rho = \frac{pM}{RT}$$

and letting $\epsilon + 2 = 3.0$ true for gases
at low pressures

$$P_T = \frac{RT}{3} \lim_{p \rightarrow 0} \frac{\epsilon - 1}{p_{mm}} = 2.097 \times 10^4 T \lim_{p \rightarrow 0} \frac{\epsilon - 1}{p_{mm}}$$

Applied to the values obtained for Fig. 6 we extrapolate at zero pressure to a $\frac{\epsilon - 1}{p}$ ratio of $5.37 \times 10^{-4} \text{ mm.}^{-1}$. The corresponding P_T value is 33.6 cc., agreeing within experimental error with previous average value of 33.4 cc.

Discussion of Results

(a) Polarization Values

Within the range of experimental error, molar polarizations calculated from the two basic equations reveal no temperature dependence. Then in the light of the given theory disulphur decafluoride must have a dipole moment indistinguishable from zero. Weight is added to this conclusion when an attempt is made to correlate the polarization values obtained by the different methods. These are seen in Table VI.

TABLE VI
SUMMARY OF MOLAR POLARIZATIONS

Compound	Liquid polarizations		Vapor polarizations
	C-M	K-O	C-M and K-O
Disulphur decafluoride	31.74	35.55	33.4
<i>n</i> -Hexane	29.77	32.30	30.04
Benzene	26.67	30.96	26.88
Toluene	33.65	39.68	34.13

It is to be noticed that the "vapor" value is slightly larger in magnitude than those resulting from liquid dielectric runs calculated from the Clausius-Mosotti expression. This is to be expected from the theoretical assumptions of Debye's theory which assumes no intermolecular action only in the case of gases and predicts anomalous discrepancies in applications to the much more highly condensed liquid molecules. Hence use of the Clausius-Mosotti equation would be expected to give slightly lower P_T values with liquids, even in the absence of any dipole moment as is observed.

In contrast, however, the molar polarization values calculated by means of the Kirkwood-Onsager equation are, in general, higher than the vapor value. It would seem that this approach tended to weight the interaction contributions a little too heavily. To indicate, however, just how normal disulphur decafluoride is in this respect, data for other nonpolar liquids are also included in the table. Polarizations have been calculated from existing dielectric constant tables (35, 36, 40) and in many cases from the original literature.

If we give the most prominent significance to those P_T values obtained with gaseous disulphur decafluoride (omitting the "out of range" 36 cc. value) and obtain their average as a representative quantitative figure, then we can make a correlation with sulphur hexafluoride and the corresponding hydrocarbons utilizing the figures of Fuoss (8) (Table VII).

It is to be noted that the dielectric molar volume is practically doubled in progression in each series, an observation tending to confirm the normal rather than the abnormal behavior of disulphur decafluoride. Secondly this conclusion is reinforced by the fact that the other three compounds also have no dipole moment.

TABLE VII
DISULPHUR DECAFLUORIDE AS A MEMBER OF THE SULPHUR FLUORIDE
HOMOLOGOUS SERIES

Compound	Polarizations, cc.		Dipole moment
	P_T	P_A	
CF_4	9.7	3.3	0
CF_3CF_3	17.2	6.4	0
SF_6	16.8	5.1	0
SF_5SF_5	33.4	12.1	0

As is often done (36), we can carry the analysis of polarizations further and evaluate the electronic and atomic contributions for the atoms and bonds involved. In Equations (I) and (II) it has been shown that $P_0 = 0$ so $P_T = P_E + P_A^*$. If we take the S-S bond P_E value obtained on organic compounds (22) as 1.73 cc. and at the same time use the S-F bond P_E value obtained on sulphur hexafluoride (36), 1.95, then

$$P_A(\text{S}_2\text{F}_{10}) = 33.37 - 1.73 - 10(1.95) = 12.14 \text{ cc.}$$

Carbon tetrafluoride, dicarbon hexafluoride, and sulphur hexafluoride can be treated in the same manner and these results are also shown in Table VII.

(b) Conduction

The low conductivity of disulphur decafluoride and its small negative temperature dependence are also significant for they indicate covalent rather than electrovalent bonding in this sulphur fluoride (19, 23) and very small dissociation of the compound (11). From these figures we can estimate the direct current specific conductance value as lying between 10^{-12} and 10^{-14} mho per cm. (41), placing disulphur decafluoride well into the "insulator" range.

(c) General

Finally, from a purely empirical point of view dielectric liquids with small dielectric constants always exhibit low conductivities. As Gemant (11) clearly points out, all compounds such as nitrobenzene, ethanol, etc., which have high dielectric constants, also possess large dipole moments. The dipoles of the solvent orient themselves radially around the individual ions, being directed by the electrical forces of these ions. In this manner they bind their true charges and diminish their free charges. The attractive forces between the ions are weakened in this way, and dissociation is made easier. The remarkable relationship between dielectric constant and conductivity thus becomes intelligible. As disulphur decafluoride has large values of neither dielectric constant nor conductivity its position is again clear.

* Owing to the toxicity and volatility of the compound determinations of its refractive index were not made.

We may say in conclusion that its electric properties establish that disulphur decafluoride is a highly stable nonpolar dielectric. The remaining evidence existing for association in the liquid state may be more apparent than real if one takes into account the high molecular weight and scanty thermal data available for disulphur decafluoride. For the present, in any case, we are left to postulate only the one electronic configuration for disulphur decafluoride—that involving two sulphur atoms linked together and in turn each surrounded by five fluorine atoms, all covalently linked.

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THE KINETICS OF THE THERMAL DECOMPOSITION OF DISULPHUR DECAFLUORIDE¹

BY W. R. TROST² AND R. L. MCINTOSH³

Abstract

The thermal decomposition of the gas disulphur decafluoride has been studied in a metal reactor. Analytical evidence showed that the reaction proceeds according to the equation $S_2F_{10} = SF_6 + SF_4$. The reaction was found to be largely homogeneous, as the heterogeneous reaction accounted for less than 5% of the total process. The homogeneous reaction was shown to be first order, and in the temperature range investigated the rate is given by $\ln k = 47.09 - 49,200/RT$. A chain reaction is postulated to explain the observed rate of the reaction. The effect of nitric oxide and acetylene dichloride on the rate and products of the reaction was investigated.

Introduction

Sulphur hexafluoride, SF_6 , and disulphur decafluoride, S_2F_{10} , are the first two and only known members of the family of saturated sulphur fluorides. Sulphur hexafluoride has been familiar since the early work of Moissan and Lebeau (9). Disulphur decafluoride, a colorless liquid boiling at $29^\circ C$., was originally prepared by Denbigh and Whytlaw-Gray (3). On the basis of an experimental parachor, they assigned a structure to this molecule in which hexavalent sulphurs are linked to each other and to five fluorine atoms by covalent bonds. Evidence in favor of this model has been obtained by Hollies and McIntosh (6), who established that disulphur decafluoride has no permanent moment.

The strength of the S-F bond in sulphur hexafluoride as calculated from thermal data given by Bichowsky and Rossini (2) is 89.9 kcal. From the dissociation of S_8 , the covalent S-S link has been evaluated as 63.8 kcal. (14), which may be taken as an upper limit to the strength of the S-S bond in disulphur decafluoride.

It is apparent that these sulphofluorides have a structure comparable to that of the hydrocarbons and the fluorocarbons. They are similar as well in that the peripheral bonds (S-F, C-H, C-F) are considerably stronger than the central bond (S-S, C-C) in each type. Significant differences between the series are the possibilities of unsaturation in the carbon compounds, and the facility with which sulphur forms stable compounds in different valence states. This combination of similarity and dissimilarity suggested that a study of the thermal decomposition of disulphur decafluoride might be a worthwhile extension of experimental kinetics.

¹ Manuscript received November 15, 1951.

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Experimental

Materials

The crude gas was purified by passage through concentrated caustic and was then fractionated until a product with a vapor pressure of 235 mm. at 0°C. and a molecular weight of 256-257 at 180 mm. pressure was obtained. Compared with reported data (3), these values indicate that the final product was 99-100% pure.

Apparatus

Since disulphur decafluoride reacts vigorously with glass or mercury at higher temperatures an inert metal reactor and metal pressure measuring instrument were required (Fig. 1). The assembly consisted of a copper cylinder R closed at the bottom end by a pressure sensitive corrugated brass diaphragm D. A liquid filler and manometer system translated the pressure of the membrane into a pressure reading. The 0.003 in. membrane D, 4 in. in diameter, covered the oil-filled diaphragm chamber C. In A, the mercury used in the U-tube F came into contact with the dibutyl phthalate used in C. The level of the mercury in F, as read from the scale N, was utilized as the null indicator. The pressures required to reproduce the null level were measured on the absolute manometer H. A slightly elevated ring E, and lead gaskets, provided an effective vacuum seal when the reactor was assembled. In practice, pressure measurements using the null method were accurate to within a millimeter.

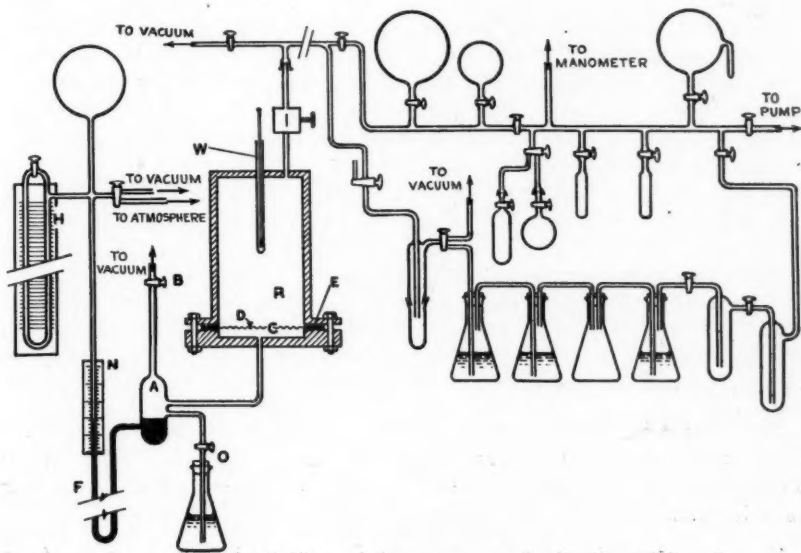


FIG. 1. Apparatus

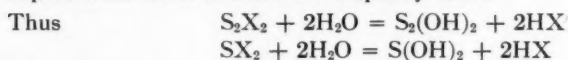
Temperature Control

The furnace consisted of two concentric thick walled magnesia cylinders heated electrically to temperatures within a few degrees of each other. By suitable manipulation of the current in the coils of the two furnaces, the temperature of the reactor, read on the thermometer W, could be kept constant within 0.1°C.

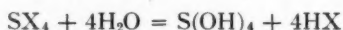
DECOMPOSITION OF DISULPHUR DECAFLUORIDE

1. Products of the Decomposition

For purposes of analysis the products of a decomposition were passed through 2*N* sodium hydroxide solution where sulphofluorides other than sulphur hexafluoride and disulphur decafluoride were removed. The latter gases were condensed out in liquid air and subsequently identified and measured by standard gas analysis methods, (fractionation, vapor pressures, molecular weights). No gases other than these passed through the caustic bubblers. Analysis of the gases that dissolved in the caustic was performed on the basis of the following information obtained from the literature for sulphur halides (12). Upon hydrolysis the sulphur halides react in a manner that would be expected for the acid halides of sulphony acids.



and by analogy



The initial products of hydrolysis are not always stable. There is eventually obtained, according to Stamm and Goehring, in the first case a mixture of free sulphur, sulphite, sulphate, and polythionates, and in the second case largely thiosulphate and a very small amount of free sulphur and sulphate. It may therefore be expected that, in the third case, largely sulphite would be obtained when solution occurs in alkali. Accordingly iodimetric titrations were carried out on aliquots taken from the sodium hydroxide solution after passage of the product gases to determine the valence state of the sulphur compounds dissolved in it. Total sulphur was determined by hydrogen peroxide oxidation and a gravimetric analysis for sulphate (9). Fluorine was measured by precipitation and separation of triphenyl tin fluoride (1). The amount of gas that was taken into solution by the caustic was calculated from *PV* data. For these gases the analytical results from 10 decompositions can be summarized in the statement

1 gas molecule = 1 atom sulphur = 4 atoms fluorine = 0.96 ion sulphite.
Experimentally this statement was never in error by more than 3%. On the above basis the gas that dissolved in caustic was presumed to be sulphur tetrafluoride.

The amounts of the gases introduced into, produced by, and recovered from the decompositions are shown in Table I.

TABLE I

RECOVERY OF SULPHUR HEXAFLUORIDE, SULPHUR TETRAFLUORIDE, AND DISULPHUR DECAFLUORIDE FROM PRODUCT GASES

Run	Moles $\times 10^3$							SA/V
	S ₂ F ₁₀ at <i>t</i> ₀	Gas at <i>t</i> _f	S ₂ F ₁₀ recov.	S ₂ F ₁₀ decom.	SF ₆ recov.	SF ₄ recov.	Gas recov.	
4	10.9	17.3	4.3	6.6	6.5	6.3	17.1	1
5	11.0	17.5	4.2	6.8	6.6	6.5	17.3	1
6	16.2	25.6	6.8	9.4	9.2	9.6	25.6	1
7	18.3	34.2	2.6	15.7	15.6	15.7	33.9	3
8	15.5	—	5.3	10.2	9.5	10.4	25.2	3
9	15.0	25.0	4.9	10.1	9.7	10.0	24.6	3

The data in columns 2 and 3 are calculated from measured pressures in the reactor at the beginning and the end of a run. Analytical data are given in the other columns. Sulphate is reported as SF₄. SF₆ and S₂F₁₀ were determined from mixed molecular weights in most instances. The reliability of this method was satisfactorily checked by fractionation of the mixture into its component parts. SA/V = surface area to volume ratio of the reaction vessel.

A comparison of columns 5, 6, and 7 shows that the decomposition may be represented by the equation



within an experimental error of about 3%. To confirm the analytical methods suitable blanks were done, such as sulphate and fluorine determinations in the presence of sodium sulphite and each other; the disulphur decafluoride loss when passed through the cold reactor and bubbler system, etc. The error as assessed from the blanks was of the order of 2%.

2. Kinetics

Experimentally the first order rate constants were to some extent dependent on the surface area to volume ratio, and on the initial pressure of disulphur decafluoride in the reactor. Rate constants were determined, therefore, for a series of runs over a wide range of initial pressures for each of three values of the surface area to volume ratio at each of three temperatures. The rate constants were calculated from the times required for half the disulphur decafluoride to decompose as shown by the pressure readings corresponding to the equation $\text{S}_2\text{F}_{10} = \text{SF}_6 + \text{SF}_4$, by means of the expression

$$k = (\ln 2)/t^{0.5}.$$

For this purpose the initial pressure had to be known accurately. With the aid of measurable values for the pressures before and after expansion into the reactor, the rate of decomposition, and the length of time required for the reactor to fill, the extrapolation was confined to a 1 mm. range, which was considered satisfactory.

The surface area was altered by the addition of fine copper wire and was geometrically estimated. For comparative purposes, the surface area to volume ratio of the unpacked reactor was assigned a value of unity. The complete pressure versus time data for a sample run are given in Table II and Fig. 2.

TABLE II*

DATA FOR A SAMPLE RUN—No. 27

P_H mm. Hg	Time, min.	Null	P_t mm. Hg	T , °Abs.
208.0	1.50	0	208.0	443.0
215.5	4.00	0	215.5	443.0
224.0	7.66	2	226.0	443.0
235.0	11.50	0	235.0	443.0
243.0	15.00	0	243.0	443.0
253.5	19.50	1	254.5	443.0
262.0	23.33	0	262.0	443.0
276.0	31.00	0	276.0	443.0
290.0	39.00	0	290.0	443.1
298.5	45.00	0	298.5	443.0
306.0	50.00	0	306.0	443.0
316.0	57.00	0	316.0	443.0
324.5	67.15	0	324.5	443.1
337.0	82.00	0	337.0	443.1
348.0	96.50	0	348.0	443.0

* P_H is the pressure read from the absolute manometer (H, Fig. 1); P_t is equal to P_H corrected for null deviations read from a millimeter scale. P_t is the pressure in the reactor at any time t .

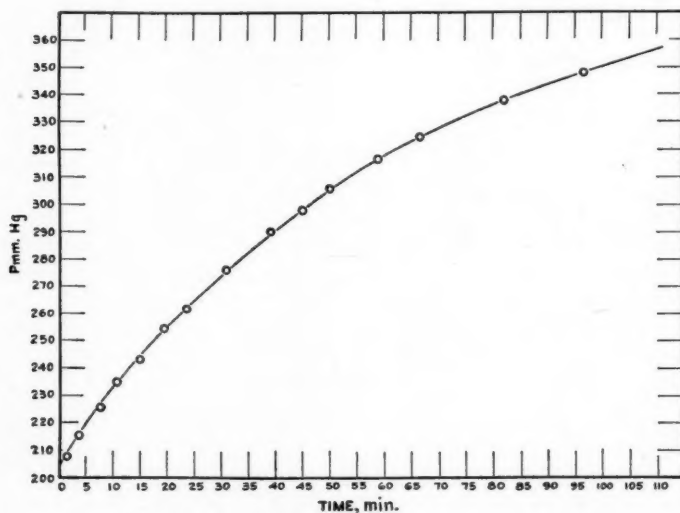


FIG. 2. Pressure vs. time curve. Temperature = 444.0° K. SA/V = 3 Run No. 27.

Altogether about sixty runs were completed under the various conditions listed above. The rate constants for these runs are given in Tables III, IV, and V, and are plotted as functions of the initial pressure and the surface area to volume ratio in Figs. 3, 4, and 5.

TABLE III
THE OVER-ALL RATE CONSTANT AS FUNCTIONS OF P_0 AND SA/V
TEMPERATURE = 434.0°A.

Run	P_0	SA/V	$k \text{ (min.}^{-1}) \times 10^3$
51	299	1	3.78
52	199	1	3.80
53	109	1	3.62
31	290	3	4.20
35	273	3	4.22
30	209	3	4.20
32	187	3	4.09
33	166	3	3.83
34	140.5	3	3.78
29	105	3	3.73
70	304	5	4.86
67	202	5	4.95
68	101	5	4.53
69	53	5	4.13
71	27.5	5	3.92

TABLE IV
THE OVER-ALL RATE CONSTANT AS FUNCTIONS OF P_0 AND SA/V
TEMPERATURE = 444.0°A.

Run	P_0	SA/V	$k \text{ (min.}^{-1}) \times 10^3$
41	317	1	11.85
42	205	1	11.75
40	180	1	11.75
43	164	1	11.80
44	150	1	11.35
45	97.0	1	11.0
46	56.0	1	11.1
47	29.8	1	10.9
19	395	3	13.90
20	300	3	13.85
28	266	3	14.00
27	204	3	13.85
17	198	3	13.80
15	186	3	14.00
14	164	3	12.80
26	154	3	12.45
25	103	3	11.35
58	300	5	15.5
59	206	5	15.2
60	172	5	14.1
61	151	5	12.8
62	126.5	5	12.1
63	103.5	5	11.6
65	69.5	5	10.9
66	32.0	5	11.0

TABLE V
THE OVER-ALL RATE CONSTANT AS FUNCTIONS OF P_0 AND SA/V
TEMPERATURE = 454.5°A.

Run	P_0	SA/V	$k(\text{min.}^{-1}) \times 10^3$
48	277	1	43.0
49	204	1	42.0
50	103.5	1	39.2
37	298	3	47.2
38	216	3	44.7
39	204	3	44.5
56	294	5	50.6
55	209	5	46.0
57	118	5	39.9
54*	217	5	46.0

* The rate constants shown in Tables III, IV, and V are no longer valid beyond 70-75% conversion. When more than this amount of disulphur decafluoride has reacted, the rate begins to fall off rapidly until, at about 85-95% conversion, reaction has practically ceased. In run 41, for example, no pressure increase was observed after 18 hr., and after 36 hr. at 444.0°K, 5% of the original amount of disulphur decafluoride had not reacted.

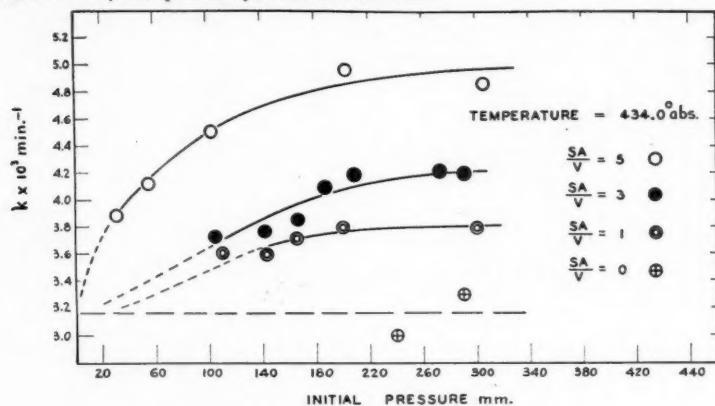


FIG. 3. Rate constants vs. initial pressure.

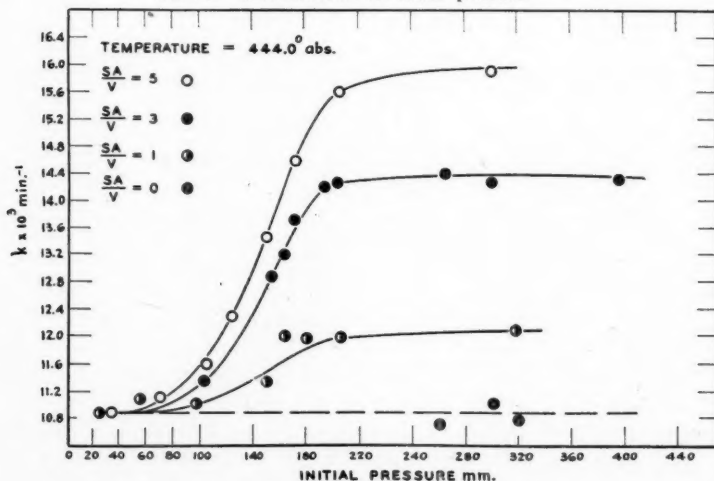


FIG. 4. Rate constants vs. initial pressure.

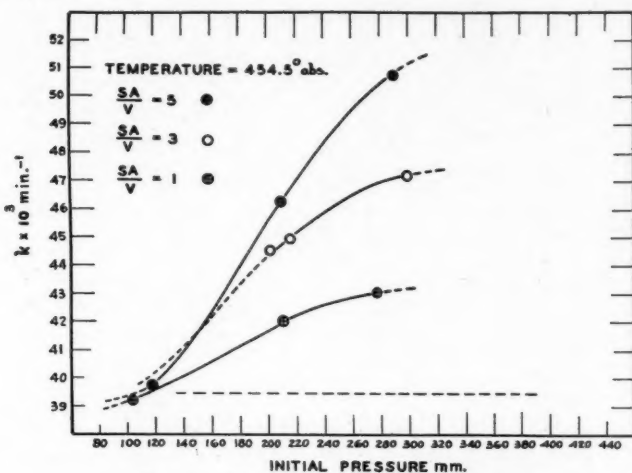


FIG. 5. Rate constants vs. initial pressure.

Separation of the Decomposition into Two Parts

Under the several conditions the over-all rate constants approach limiting values at high pressures. Assuming a roughly linear relationship between the surface area to volume ratio and the extent of the surface dependent reaction, a rate constant for the homogeneous decomposition may be obtained from an extrapolation of the limiting rates to $SA/V = 0$. These data are shown in Table VI.

TABLE VI
TEMPERATURE DEPENDENCE OF RATE CONSTANTS
MAXIMUM RATE CONSTANTS FOR THE DIFFERENT VALUES OF SA/V

Temp., °abs.	$SA/V=5$ k_5	$SA/V=3$ k_3	$SA/V=1$ k_1	$SA/V=0$ k_0
434.0	0.00491	0.00420	0.00380	0.00318
444.0	0.0153	0.0139	0.0118	0.0109
454.5	0.0506	0.0472	0.0430	0.0400

The values of the rate constants for the homogeneous reaction may be checked independently. At low pressures the over-all rate constants again become independent of pressure, but in this region they are unaffected by changes in the surface area, see Figs. 4 and 5. Within experimental error, the low pressure homogeneous rate constants are identical with those calculated by the extrapolation method above.

*Temperature Dependence of Decomposition**(a) Homogeneous Reaction*

The logarithms of the rate constants for the four surface area to volume ratios are plotted against the reciprocals of the absolute temperatures in Fig. 6, and the corresponding Arrhenius activation energies are given in Table VII.

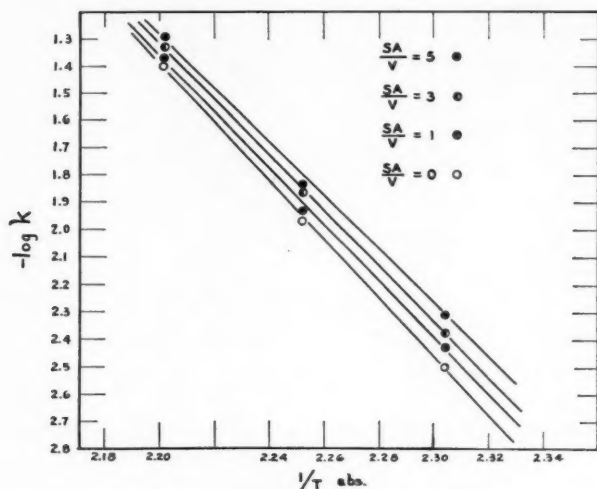


FIG. 6. Temperature dependence of rate constants.

TABLE VII
TEMPERATURE DEPENDENCE OF RATE CONSTANTS
ACTIVATION ENERGIES COMPARED WITH SA/V

SA/V	E (cal./mole)
5	44,800
3	46,500
1	47,800
0	49,200

With an activation energy of 49,200 cal. per mole, the absolute rate of the homogeneous decomposition in the range 160–180°C. may be expressed as

$$\ln k = 47.09 - 49,200/RT. \quad (1)$$

(b) Heterogeneous Reaction

Assuming that a homogeneous first order decomposition occurs to the extent expressed in Equation (1), the temperature dependence of the remaining part of the reaction may be estimated. The slopes of the Arrhenius plots derived from the times and temperatures at which 5% of the total reaction has taken place on the surface, as obtained from the excess of the over-all as compared with the homogeneous rate, give values of 39 to 40 kcal. per mole for the activation energy of the heterogeneous reaction.

3. Effect of Foreign Gases

(a) Nitric Oxide

The effect of nitric oxide, in amounts from 0.1 to 4%, on the decomposition of disulphur decafluoride at 444°C., was studied in six runs at two different values of SA/V , 1 and 5. The initial pressures were about 200 mm. These kinetic data are assembled in Table VIII and Fig. 7.

TABLE VIII
KINETIC DATA FOR THE DECOMPOSITION OF DISULPHUR DECAFLUORIDE IN THE PRESENCE OF
NITRIC OXIDE

$P_0 = 200$ mm.		Temperature = 444.0°A.		
Run	%NO	SA/V	$k_{obs.}$	K_{NO} (SA/V=1)
	0	1	0.0118	0.0118
78	0.1	1	0.0120	0.0120
77	0.5	1	0.0141	0.0141
76	1.0	1	0.0172	0.0172
73	1.0	5	0.0216	0.0168
74	2.0	5	0.0265	0.0208
72	4.0	5	0.0314	0.0256

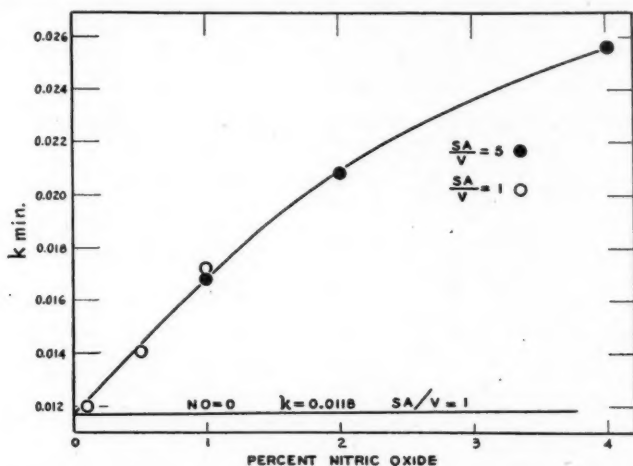


FIG. 7. Rate constants vs. per cent nitric oxide. Temperature = 444.0°K.

The values of the first order constants, as measured from the pressure-time curves developed for the runs, are given in column 4. In column 5, a rate constant, k_{NO} , is listed. These constants were obtained by correcting for the extra surface in the reactor, when it was packed.

(b) *Acetylene Dichloride*

The per cent concentrations of acetylene dichloride are given with the kinetic data for these runs in Tables IX and X, Figs. 8 and 9.

(c) *Order of the Catalyzed Reactions*

The first order rate constants, calculated at various times in the course of reactions catalyzed by nitric oxide and acetylene dichloride are given in Table XI.

(d) *Analytical Data for Catalyzed Reactions*

The products of the catalyzed decompositions were determined analytically in the same way as previously reported for the uncatalyzed reactions. Within

TABLE IX

KINETIC DATA FOR THE DECOMPOSITION OF DISULPHUR DECAFLUORIDE IN THE PRESENCE OF ACETYLENE DICHLORIDE

$P_0 = 200$ mm.		$SA/V = 1$	
Run	Temp., °A.	% $C_2H_2Cl_2$	k
79	444.0	4	0.0179
80	444.0	3	0.0160
—	444.0	0	0.0118
81	454.5	4	0.0633
82	454.5	3	0.0543
—	454.5	0	0.0410

TABLE X

ACTIVATION ENERGIES FOR THE ACETYLENE DICHLORIDE CATALYZED DECOMPOSITION OF DISULPHUR DECAFLUORIDE

% $C_2H_2Cl_2$	Activation energy, cal./mole
4	49,000
3	48,000
0	47,800

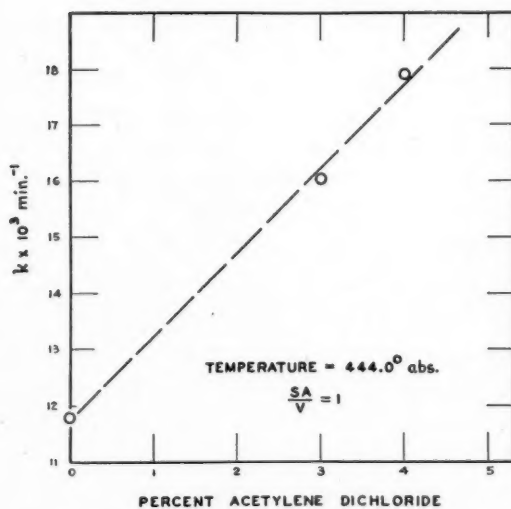


FIG. 8. Rate constants vs. per cent acetylene dichloride.

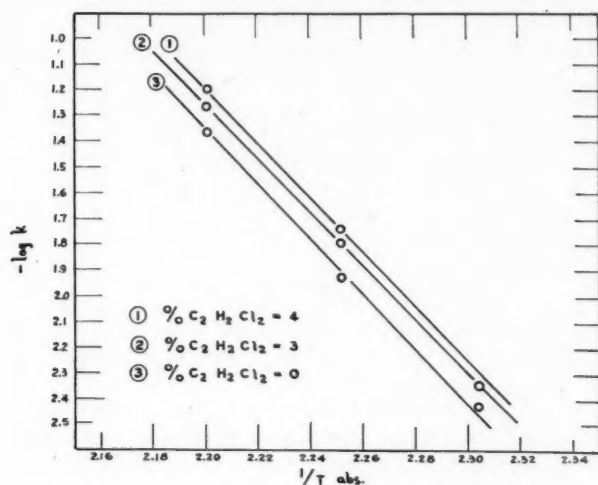


FIG. 9. Temperature dependence of the catalyzed decomposition of disulphur decafluoride.

TABLE XI
RATE CONSTANTS VS. TIME FOR CATALYZED REACTIONS

Run No. 79 4% C ₂ H ₂ Cl ₂		Run No. 76 1% NO	
Time, min.	<i>k</i> min. ⁻¹	Time, min.	<i>k</i> min. ⁻¹
3	0.0173	2	0.0186
6	0.0181	4	0.0190
9	0.0175	6	0.0185
12	0.0179	8	0.0185
24	0.0185	10	0.0188
33	0.0179	20	0.0185
42	0.0179	30	0.0176
		40	0.0172

the experimental error, the end products were unaltered by the presence of catalyst. The data are assembled in Tables XII and XIII, in terms of sulphur hexafluoride and sulphur tetrafluoride recovered, and disulphur decafluoride reacted. The recovery of the catalyst itself was confirmed only qualitatively.

TABLE XII
ANALYTICAL DATA ON CATALYZED RUNS. NITRIC OXIDE
TEMPERATURE = 444.0°C.

Run	% Nitric oxide	S ₂ F ₁₀ dec.	SF ₆ recov.	SF ₄ recov.
77	0.5	5.9	5.9	6.1
78	0.1	9.6	9.4	9.4

TABLE XIII

ANALYTICAL DATA ON CATALYZED RUNS. ACETYLENE DICHLORIDE

Run	% C ₂ H ₂ Cl ₂	S ₂ F ₁₀ dec.	SF ₆ recov.	SF ₄ recov.	Temp. °K.
79	4	6.5	6.6	6.1	444.0
80	3	6.5	6.3	6.2	444.0
81	4	5.9	6.0	6.0	454.5
82	3	7.2	6.9	7.1	454.5

Discussion

The kinetic data, Figs. 3, 4, and 5, suggest that a homogeneous reaction with a first order rate independent of the pressure over the range 25–400 mm., and a heterogeneous reaction, the extent of which varies with temperature, pressure, and perhaps degree of conversion, together make up the over-all reaction. As the surface dependent reaction forms not more than 5–10% of the total decomposition in the unpacked reactor, the rate constants calculated for the homogeneous decomposition cannot be far in error.

The Homogeneous Decomposition

The absolute rate of the homogeneous decomposition may be expressed in the form

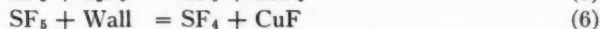
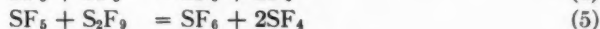
$$k = 2.99 \times 10^{20} e^{-49,200/RT} \text{ min.}^{-1}$$

over the temperature range 433 to 455°K. The value of the frequency factor, 2.99×10^{20} , is quite large compared with the values obtained for this constant in other unimolecular decompositions (4, 11). For first order reactions which may be explained as unimolecular rearrangements on the basis of the Lindemann mechanism (8) and an activation energy term expressed in n degrees of freedom as developed by Kassel (7), Hinshelwood (5) and others, frequency factors of the order of magnitude of 10^{16} are obtained. This value is deficient for the present case by a factor of 10,000. It is evident then, that a description of the decomposition of disulphur decafluoride as a unimolecular rearrangement is inadequate.

Chain Reactions in the Decomposition of Disulphur Decafluoride

It is possible to formulate a series of reactions involving a free radical chain to explain the decomposition of disulphur decafluoride. There is, however, outside of the exceptionally large value of the velocity constant, and the marked fall-off in rate at high conversions, nothing to indicate the presence of chains.

If the initial cleavage in the thermal degradation of an disulphur decafluoride molecule is assumed to be the symmetrical breaking of the S–S bond, two SF₅ free radicals would be released that may be considered capable of inducing the decomposition of further disulphur decafluoride molecules in a manner similar to the rather arbitrary selection of reactions below.



In 1 to 7 the chains are initiated by 1, propagated by a rapid repetition of 2 and 3, and terminated by 4, 5, and 6. In association with these a unimolecular decomposition 7 may be present. Disulphur decafluoride* represents an activated molecule.

As the surface increased the over-all rate it will be assumed that 6 may be ignored as a chain breaking reaction.

No reactions involving free fluorine atoms have been considered as, in the first place, the bonds involved have large energies and, secondly, no fluorine is formed in the decomposition.

Other possibilities than 1 to 7 could be suggested, but as these are adequate to explain a chain reaction and already include two compounds, SF_5 and S_2F_9 , evidence for which is quite lacking, the list will not be extended.

From the usual steady state treatment for the above scheme,

$$(\text{S}_2\text{F}_9) = \frac{k_2(\text{SF}_5)(\text{S}_2\text{F}_{10})}{k_3 + k_5(\text{SF}_5)} \quad (8)$$

Using 8 to substitute into the expression for $d(\text{SF}_5)/dt$ and equating this to zero there is obtained

$$\frac{2k_4k_5(\text{SF}_5)^3}{(\text{S}_2\text{F}_{10})} + \frac{2k_3k_4(\text{SF}_5)^2}{(\text{S}_2\text{F}_{10})} + 2k_2k_5(\text{SF}_5)^2 - 2k_1k_5(\text{SF}_5) - 2k_1k_3 = 0. \quad (9)$$

The first two terms in 9 include the concentration of S_2F_{10} . (SF_5) is certainly very small compared with $(\text{S}_2\text{F}_{10})$. These two terms may then drop out, leaving a quadratic and therefore a simple solution.

This consideration is not valid at high conversions, and experimentally the rate fell off rapidly at low per cent concentration of disulphur decafluoride. With these eliminations (SF_5) may be solved for

$$(\text{SF}_5) = \frac{k_1}{2k_2} + \left[\frac{(k_1)^2}{(2k_2)} + \frac{(k_1k_3)}{(k_2k_5)} \right]^{1/2} \quad (10)$$

The rate of disappearance of disulphur decafluoride in this scheme is given by

$$\frac{d(\text{S}_2\text{F}_{10})}{dt} = -k_1(\text{S}_2\text{F}_{10}) - k_2(\text{S}_2\text{F}_{10})(\text{SF}_5) - k_7(\text{S}_2\text{F}_{10}). \quad (11)$$

Making the appropriate substitutions in (11), a first order rate constant is obtained for the over-all reaction.

$$\frac{d(\text{S}_2\text{F}_{10})}{dt} = -(\text{S}_2\text{F}_{10}) \left(k_7 + \frac{3k_1}{2} + \frac{(k_1)}{(2)} + \frac{k_1k_2k_3}{k_5} \right) \quad (12)$$

$$\text{and where } k = \left(k_7 + \frac{3k_1}{2} + \frac{(k_1 + \frac{k_1 k_2 k_3}{k_5})^{\frac{1}{2}}}{2} \right) \quad (13)$$

$$\text{then } \frac{d(\text{S}_2\text{F}_{10})}{dt} = -k(\text{S}_2\text{F}_{10}), \quad (14)$$

as required. Unless further extreme assumptions are made, 12 cannot be reduced to a simpler form. In this sense three possibilities exist. The whole reaction may proceed according to reaction 7, a case which has been discussed and does not seem satisfactory. Again, a chain decomposition may constitute the entire reaction, as Rice and Herzfeld suggested for the decomposition of ethane (11). In this circumstance $k_7 = 0$, and if k_1 , the chain initiating rate, is small compared with the chain propagating rates k_2 and k_3 , then

$$\frac{d(\text{S}_2\text{F}_{10})}{dt} = \left(\frac{k_1 k_2 k_3}{k_5} \right)^{\frac{1}{2}} (\text{S}_2\text{F}_{10}). \quad (15)$$

In this instance some meaning could be given to activation energies for

$$\frac{E_1 + E_2 + E_3 - E_5}{2} = E = 49,200 \text{ cal. per mole.} \quad (16)$$

16 is not a severe restriction. Reaction 5 represents a radical recombination and E_5 may then be quite small. If this is true, Equation (16) will probably be satisfied if $E_1 + E_2 + E_3$ is approximately equal to 100 kcal. Speculative values to satisfy this condition seem reasonable.

The magnitude of the frequency factor, 2.99×10^{20} , eliminates the possibility that the entire decomposition occurs by means of a unimolecular rearrangement. But reaction (7) could still contribute to the decomposition. In this case, the rate equations (12) and (13) could not be simplified. But the important characteristics of the decomposition, the large frequency factor, the first order rate, the rate fall-off at high conversions, the reaction products, and the size of the activation energy, would still be satisfied if reaction (7) accompanied the chain reaction.

Homogeneous Catalysis in the Decomposition of Disulphur Decafluoride

The addition of particular catalytic agents to a decomposition that consists of chain and/or nonchain parts may increase or decrease the rate of reaction (14). Presumably the catalyst can, among other things, either initiate chains or terminate them.

The information obtained from the decomposition of disulphur decafluoride when catalyzed by nitric oxide, and by acetylene dichloride, can be summarised as follows:

- i. In both cases, the increase in rate was proportional to the amount of catalyst added, in the concentration range 0 to 4% catalyst.
- ii. Good first order rates were obtained, indicating that the catalyst was not consumed during the course of the reaction.
- iii. The experimental activation energy for the acetylene dichloride reaction

- was indistinguishable from that for the uncatalyzed decomposition. Nitric oxide was used only at one temperature.
- iv. 2% nitric oxide doubled the rate. It was the more efficient catalyst by a factor of about 4.
 - v. The catalysis occurred in the gas phase as it was independent of the surface area to volume ratio.
 - vi. The nature and products of the decomposition were apparently unaffected by the presence of catalyst.

It is generally believed that a catalyst acts in a manner which permits a reaction with a simpler mechanism and a lower activation energy, and therefore a larger rate, to augment or displace the uncatalyzed reaction (13). However, if the data summarized in (i) to (vi) are reliable, the catalyzed decompositions could not have differed greatly from the uncatalyzed reactions in either mechanism or activation energy. If the reaction occurs solely by means of the rupture of the S-S bond in activated S_2F_{10} to give two SF_5 particles and the subsequent chain reactions of these particles, such a catalysis as was observed can occur only if the chains are lengthened or an additional reaction occurs between the catalyst and activated S_2F_{10} to produce more SF_5 free radicals. It is not likely that chains could be lengthened to the extent required.

A Possible Mechanism for the Decomposition of Disulphur Decafluoride

It will be assumed as is suggested by the data, that the disulphur decafluoride molecules decomposing to give SF_5 particles are activated to the same extent whether or not catalyst is present. Then, following a collision between an activated S_2F_{10} molecule and a catalyst molecule, unless a deactivating collision intervenes when no chemical reaction occurs, one or two SF_5 free radicals are produced and the catalyst is finally regenerated. This is analogous to the mechanism suggested for unimolecular rearrangements in the gas phase, and may therefore be compared with



If reactions 1 and 7 both contribute to the decomposition, an accelerated rate would result from any increase in the ratio of 1 to 7. In this circumstance a particular effect of a catalyst molecule upon a disulphur decafluoride molecule could be interference with the fluorine transfer as involved in 7, limiting the reaction to a rupture of the S-S bond, as in 1. If the catalyst were not consumed during the reaction, the products of the decomposition would be independent of the presence of catalyst. In addition, if the chain propagating reactions of SF_5 were rapid compared with the rate at which activated S_2F_{10} were consumed by 1 and 7, such a catalytic increase of the experimental rate would have little effect on the Arrhenius activation energy. The contribution of reaction 7 to the measured values of the absolute rate, as it does not involve a chain, will likely be very small, particularly as rather long chains are required to rationalize the speed of the reaction.

Such a mechanism may explain the results obtained in this work. As a further check the several minimum chain lengths involved may be estimated.

The uncatalyzed homogeneous decomposition may be considered. It will be assumed that the expression developed by Hinshelwood (5)

$$\frac{Z \cdot e^{\frac{-E_0}{RT}} \left(\frac{E_0}{RT} \right)^{\frac{n}{2}-1}}{\left(\frac{n}{2} - 1 \right)!} \quad (17)$$

gives a rough measure of the rate at which activated S_2F_{10} molecules may decompose by means of an S-S bond split. Here Z is the collision frequency, with the molecular diameter taken as 10^{-7} Å.; $E = 49.2$ kcal., $E_0 = 63.8$ kcal (reference 10); and $n/2 = 16$, evaluated from $E + \left(\frac{n}{2} - 1 \right) RT = E_0$.

(17) will be more nearly true the lower the pressure, and at 30 mm. pressure is equal to $10^{11.9}$ molecules per cc. per sec. The total number of molecules that decompose per cubic centimeter per second when calculated from the observed reaction rate at 30 mm. is $10^{14.1}$. Then for every molecule of disulphur decafluoride that decomposes because of a rupture of the S-S bond, $10^{4.1-11.9} = 10^{2.2}$ decompose by some other mechanism. If this is the result of a chain reaction the minimum chain length is equal to 80 at 30 mm. as two SF_6 free radicals may arise from each molecule of S_2F_{10} .

With regard to the catalyzed decompositions, the minimum chain length is given by the number of molecules that do react as the result of catalysis, divided by the largest number of collisions between the catalyst and the reactant that could result in decomposition. Only collisions between activated S_2F_{10} and catalyst molecules count. Therefore a minimum chain length may be estimated by dividing ΔkN by an expression identical with (17) except that z now refers to the collision frequency between catalyst and disulphur decafluoride. Δk is the catalytic increase in first order rate and N = molecules of disulphur decafluoride per cubic centimeter. The number that comes out of these manipulations is 1500. With the suggested mechanism, however, this number corresponds to a product value for two chains. Thus if one catalyst molecule participates in x collisions fruitful with respect to SF_6 production, and each of these SF_6 free radicals is subsequently involved in the decomposition of y molecules of S_2F_{10} as in reactions 2 and 3, then

$$2 \cdot x \cdot y = 1500. \quad (18)$$

The minimum value for y as estimated from (17) for pure disulphur decafluoride at 30 mm. is certainly in as good agreement with (18) as could be expected, where x is unknown but likely much larger than 1, at 200 mm. disulphur decafluoride. At this pressure the required reaction rate is obtained if about half of the activated S-S bond ruptures give SF_6 particles. It is true that this agreement is in no way conclusive, as the assumptions involve the applicability of the Maxwell distribution in n square terms, as well as uncertifiable values of activation energies and molecular diameters.

It is more difficult to suggest a simple mechanism for catalysis in the decomposition if reaction 7 is absent. If it is possible for a collision with a catalyst molecule to decrease the length of time required for an activated S_2F_{10} molecule to give 2 SF_6 particles, catalysis would occur. Although the picture is vague, the experimental results obtained in this work could perhaps be explained as well in some such manner.

Acknowledgments

The authors wish to thank Dr. O. Maass for his co-operation, and for the use of his laboratory; and the National Research Council of Canada, for Grants-in-Aid.

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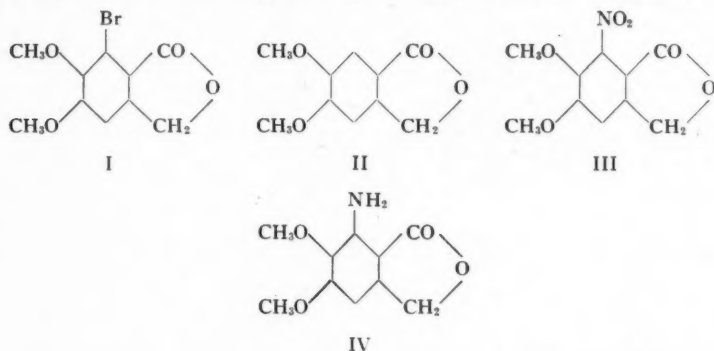
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3-BROMOMETAMECONINE¹BY R. H. MANSKE,² J. A. McRAE,³ AND R. Y. MOIR³

Abstract

3-Bromo-*m*-meconine was prepared in three ways: (a) by direct bromination of metameconine, (b) from 5-bromoveratric acid and formaldehyde, and (c) from 6-amino-*m*-meconine by a method which amounted to an independent derivation of the structures of 6-amino-*m*-meconine and its products of transformation. The structures obtained agreed with those previously reported by us. Carefully purified 6-bromo-*m*-meconine was found to melt at 207°C. in agreement with our previous work, rather than at 223°C. as reported by Rây and Robinson. During the investigation, a convenient synthesis of metaopianic acid was discovered, and the following new compounds were characterized: 6-acetamino-*m*-meconine, 6-diacetylamino-*m*-meconine, 6-acetamino-3-bromo-*m*-meconine, 6-amino-3-bromo-*m*-meconine, 2-iodoveratric acid, and 5-iodoveratric acid.

In a recent paper (10), it was shown that there had been some uncertainty about the nature of the compound regarded as 6-bromo-*m*-meconine (I).



This compound had been prepared by Rây and Robinson (17) from *m*-meconine (II) through the stages of nitration, reduction, and Sandmeyer replacement of the amino group by bromine, and was reported to melt at 223°C. Repeated attempts to confirm their work invariably yielded a bromo-*m*-meconine melting at 207°C. (10), and the same lower melting point was obtained when the synthesis was once more repeated with special precautions to ensure the purity of all the compounds, although the intermediate 6-nitro-*m*-meconine (III) and 6-amino-*m*-meconine (IV) had almost the same melting points as those reported by Rây and Robinson (17). Furthermore, these authors stated (17) that the condensation of 2-bromoveratric acid (V) with formaldehyde gave the same 6-bromo-*m*-meconine melting at 223°C. This was essentially their proof of

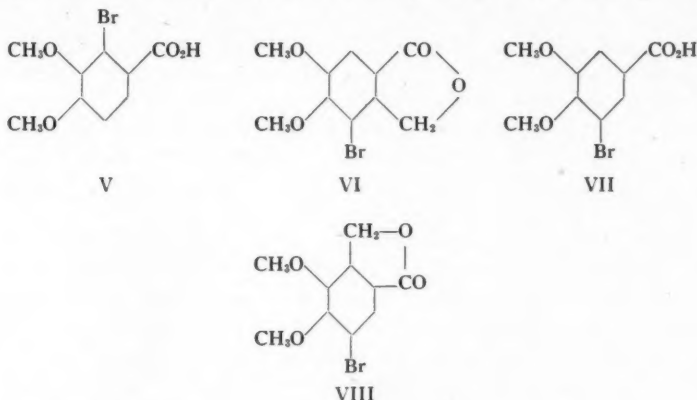
¹ Manuscript received November 14, 1950.

Contribution from the Research Laboratories, Dominion Rubber Company, and from the Department of Chemistry, Queen's University.

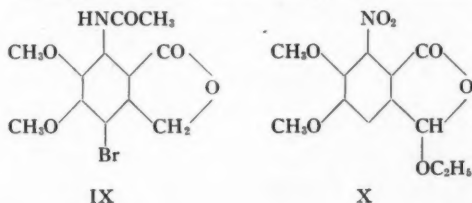
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orientation. Our attempts to prepare 6-bromo-*m*-meconine by this method did not give it although a small yield of a product of melting point 223°C. was usually obtained. The structure of this compound is under investigation.



Since only two ring-brominated bromo-*m*-meconines are possible, preparation of the alternative 3-bromo-*m*-meconine (VI) was of some importance. The compound has now been prepared by three different routes. First of all, 5-bromoveratric acid (VII) when condensed with formaldehyde gave a small yield of a compound melting at 183°C. which might have been either 3-bromo-*m*-meconine (VI) or its isomer (VIII). However, reductive elimination of the bromine yielded *m*-meconine and therefore only structure VI was possible. Secondly, direct bromination of *m*-meconine yielded the same compound, and since I cannot be obtained from 5-bromoveratric acid by condensation with formaldehyde, nor VIII by bromination of *m*-meconine, structure VI was confirmed. Thus bromination and nitration occur at different positions on the ring. Finally, the 6-amino-*m*-meconine (IV) of Rây and Robinson (17) was acetylated and then brominated, and the resulting 6-acetylamino-3-bromo-*m*-meconine (IX) deacetylated and the amino group eliminated *via* the diazo

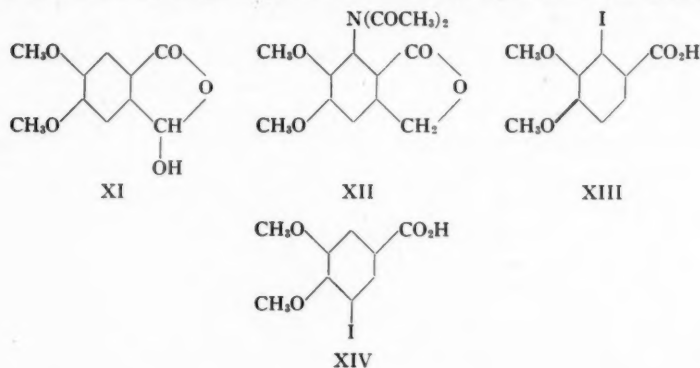


compound with the aid of hypophosphorous acid. The resulting bromo-*m*-meconine was identical with the product (VI) obtained by the above two independent routes. This series of reactions confirmed the orientation of 6-amino-*m*-meconine which previously (10) had been obtained by bringing it into relation with 3-methoxy-*m*-meconine (1, 9). Both the 6-bromo-*m*-meconine of

melting point 207°C. and the 3-bromo-*m*-meconine of melting point 183°C. have been oxidized to the same 3-bromo-*m*-hemipinic acid (5), a further confirmation of the structures assigned to them.

A number of other points had to be considered before the structures of the bromo-*m*-meconines could be finally assigned. For example, it may be noted that our structures are not independent of the proper orientation of *m*-meconine and of the bromoveratric acids. The structure of *m*-meconine has been firmly established (4, 12), while the correct orientation of the bromoveratric acids has been thoroughly verified by the work of a number of chemists (2, 3, 7, 8, 11, 14, 15, 18, 19). At various times it seemed possible that some of the compounds regarded as *m*-meconines might actually be pseudo-esters of *m*-opianic acid. For example, Rây and Robinson (17) prepared 6-nitro-*m*-meconine (III) by the action of nitric acid upon *m*-meconine and purified the crude, acid-contaminated product by extraction with boiling alcohol. These conditions seemed favorable (4, 6) for the formation of the pseudo-ester (X) whose carbon content is not very different from that of III. The point was easily settled since 6-nitro-*m*-meconine prepared out of all contact with ethanol was identical with the material made by the method of Rây and Robinson. By various means, the other compounds were also shown not to be derivatives of *m*-opianic acid.

There is recorded in the experimental section a convenient synthesis of *m*-opianic acid (XI) (4, 6, 13) from *m*-meconine, as well as the characterization of the new compounds 6-diacetylamino-*m*-meconine (XII), 2-iodoveratric acid (XIII), and 5-iodoveratric acid (XIV) which were incidental to the main portion of our work. Investigation of other substituted *m*-meconines is in progress.



Experimental

All melting points were corrected.

3-Bromo-*m*-meconine (VI)

The procedure was similar to that used by Rây and Robinson (17) for the production of *m*-meconine. Acetic acid (40 cc.), formaldehyde (7 cc. of a 35% solution), concentrated hydrochloric acid (20 cc.), and 5-bromoveratric acid

(7 gm.) were heated on the steam bath intermittently for a total of 54 hr.; at the end of the first 30 hr. of heating another portion of formaldehyde solution (5 cc.) and a portion of acetyl chloride (5 cc.) were added. At the end of the heating period, the mixture was diluted with much ether and the ethereal solution thoroughly washed with water. Washing with sodium bicarbonate solution served to remove the unchanged bromoveratric acid (2.8 gm.) from the ethereal solution, which was then evaporated to dryness. Three crystallizations of the residue from methanol gave an almost pure product of melting point 178°C. which had a carbon and hydrogen content in fairly close agreement with the theoretical for 3-bromo-*m*-meconine. Reduction of a portion of this material with zinc and aqueous potassium hydroxide yielded a substance of melting point 154–155°C. which proved to be identical with *m*-meconine. Oxidation of the bromo-*m*-meconine with permanganate and treatment of the product with diazomethane gave the dimethyl ester of 3-bromo-*m*-hemipinic acid (5, 10).

In another preparation on a larger scale, 5-bromoveratric acid (71.8 gm.) was heated for 28 hr. on the steam bath with glacial acetic acid (250 cc.), concentrated hydrochloric acid (174 cc.), and formaldehyde (60 cc. of a 40% solution). Water (100 cc.) was then added and the yellow-brown precipitate immediately recovered. Fractional crystallization of this precipitate from dilute ethanol gave 3-bromo-*m*-meconine, m.p. 182.4–182.8°C., and 5-bromoveratric acid, m.p. 189.5–190°C. The filtrate of the reaction mixture was concentrated and yielded considerable amounts of a new substance which after five recrystallizations formed white needles of m.p. 240.5–242°C. The constitution of this material is still under investigation.

A crude sample of the 3-bromo-*m*-meconine (m.p. 178–178.5°C., 6.80 gm.) made in the above reaction was later purified by successive recrystallizations from methanol and glacial acetic acid. Large, colorless needles of m.p. 181.9–183.6°C. were obtained in a yield of 4.64 gm. Calc. for $C_{10}H_9O_4Br$: C, 43.96%; H, 3.30%. Found: C, 43.61%; H, 3.33%.

meta-Meconine (II)

Veratric acid (402.6 gm.) was converted to *m*-meconine essentially by the method of Rây and Robinson (17). The crude *m*-meconine was very thoroughly extracted with aqueous sodium bicarbonate solution, in which it was insoluble, and then with water. After being dried, the extracted crystals were twice recrystallized from *n*-butanol, distilled at 175–185°C. (0.1 to 0.2 mm.), once again recrystallized from *n*-butanol, and finally dried *in vacuo* over sulphuric acid. The pure white crystals of 'purified *m*-meconine' weighed 149.1 gm. (35% yield); m.p. 157.1–157.5°C. Two other crops of less pure *m*-meconine were also obtained: one from the mother liquors by distillation *in vacuo* and two crystallizations from *n*-butanol, yield 30.5 gm. or 7%, m.p. 151–156°C.; the other from various tars obtained in the experiment by extraction with much hot water, recovery of the soluble crystals, extraction of the crystals with sodium

bicarbonate solution, distillation, and recrystallization. The yield of impure *m*-meconine obtained from the tars in this way was 14.1 gm., or 3%, m.p. 151–155°C. The tars themselves were quite lachrymatory, pointing to the presence of chloromethyl groups. Veratric acid was recovered in very small amounts in a very impure condition.

Bromination of m-Meconine

m-Meconine (purified as above, 50.0 gm.), glacial acetic acid (508 cc.), bromine (13 cc.), iron powder (0.1 gm.), and aluminum metal (0.1 gm.) were mechanically stirred together and heated intermittently over the course of several days at about 40–83°C. for 27 hr. altogether; the temperature during the heating periods was usually 50–60°C. Then more bromine (1.8 cc.) dissolved in glacial acetic acid (5 cc.) was added. Next morning the reaction mixture was rinsed onto much ice and brought to neutrality with sodium hydroxide, sodium bisulphite, and water. The precipitated solid was recovered, thoroughly extracted with dilute hydrochloric acid, with aqueous sodium bicarbonate, and with water, and dried in the air. The crude crystals (57 gm.) were fractionally recrystallized from methanol. Several fractions of low melting point were obtained, as well as four fractions which melted above 179°C. and so were already almost pure. The four fractions of high melting point were combined (yield 7.9 gm. or 11%), and recrystallized several times, once from methanol and three times from glacial acetic acid, charcoal being used once. The glistening white crystals (3.0 gm.) so obtained had a melting point of 182.3–183.2°C. Calc. for $C_{10}H_9O_4Br$: C, 43.96; H, 3.30%; molecular weight 273. Found: C, 43.76, 44.15; H, 3.49, 3.54%; molecular weight by Rast camphor method: 279. Since the mother liquors from the four final crystallizations yielded 3.3 gm. of product of m.p. 180.9–182.4°C., it seemed that the analyzed product must have been pure. A mixed melting point showed that the analytical material was identical with the 3-bromo-*m*-meconine obtained from the reaction of 5-bromoveratric acid and formaldehyde.

Prolonged attempts were made to separate pure compounds from the crystalline fractions of low melting point, but after fractional distillation, fractional crystallization from *n*-butanol, and sublimation of the crystals, a number of impure fractions were obtained which all melted approximately in the range 130–150°C.

6-Nitro-m-meconine (III)

The method was that of McRae *et al.* (10), except that the use of ethanol was avoided to prevent confusion of the product with the ethyl pseudo-ester of 6-nitro-*m*-opianic acid. *m*-Meconine (purified, as above, 30.1 gm.) was added with mechanical stirring to a cooled mixture of concentrated nitric acid (170 cc.) and concentrated sulphuric acid (38 cc.), the temperature being kept below 8°C. Stirring was continued for one hour, then the mixture was kept below 5°C. for three hours, and finally poured onto ice (1200 gm.) with stirring. Next morning, the cream-colored crystals were recovered and very thoroughly ex-

tracted with water to remove the inorganic acids as completely as possible. The wet crystals were then twice recrystallized from glacial acetic acid. After the first recrystallization, the very large, very slightly yellow needles were washed only with acetic acid, but, after the second, they were washed with acetic acid and then repeatedly with methanol before being thoroughly dried. The yield of pale yellow needles of m.p. 182.3–183.1°C. was 26.6 gm. or 72%. Calc. for $C_{10}H_9O_4N$: C, 50.21; H, 3.77%. Found: C, 50.69, 50.43; H, 3.91, 3.81%.

6-Amino-*m*-meconine (IV)

Pure 6-nitro-*m*-meconine (25.8 gm.), made from pure chemicals, was converted to crude 6-amino-*m*-meconine by the method of Rây and Robinson (17). The crude amine was twice recrystallized from methanol with the help of 'Filter-Cel', giving beautiful white needles of m.p. 160.0–160.6°C., yield 14.4 gm. or 64%. Calc. for $C_{10}H_{11}O_4N$: C, 57.41; H, 5.26%. Found: C, 57.48, H, 5.10%.

6-Acetamino-*m*-meconine

(1) Pure 6-amino-*m*-meconine (10.0 gm.), made from pure chemicals, was dissolved in warm glacial acetic acid (55 cc.) and treated with acetic anhydride (7.0 cc.). The solution was kept at 72–84°C. for 40 min., cooled with shaking, diluted with water (65 cc.) and chilled. White crystals separated and were recovered and thoroughly washed with water. After one recrystallization from water, the pure crystals had a melting point of 228.3–230.0°C., yield 5.0 gm. or 42%.

(2) Crude 6-amino-*m*-meconine (13.6 gm.) made during the previous investigation (10) was converted to the crude acetyl derivative in the same way as just described. The crude product was recrystallized twice from glacial acetic acid, charcoal being used once; the crystals so obtained weighed 3.1 gm., m.p. 229.3–230.3°C. One more recrystallization from water gave the analytical sample in large colorless plates, m.p. 229.8–230.4°C. Calc. for $C_{12}H_{13}O_5N$: C, 57.37; H, 5.18; OCH_3 , 24.70%. Found: C, 57.73, 57.99; H, 5.10, 5.16; OCH_3 , 24.72, 24.64%. A mixed melting point with the material made from the pure chemicals showed no depression, so that the identity of the 6-amino-*m*-meconine used previously (10) was firmly established. Additional amounts of the acetyl derivative were recovered from the mother liquors.

6-Diacetylamino-*m*-meconine (XII)

Crude 6-acetamino-*m*-meconine (0.91 gm.) was heated under reflux for five hours with acetic anhydride (11.2 cc.). The solution was chilled in a bath of ice and salt and the crystals which separated were recovered and washed with water. After one recrystallization from dilute acetic acid, the glistening white crystals had a melting point of 202.6–203.8°C. Calc. for $C_{14}H_{15}O_6N$: C, 57.34; H, 5.12; OCH_3 , 21.16%. Found: C, 57.28, 57.59; H, 5.01, 5.22; OCH_3 , 21.34, 21.25%.

6-Acetamino-3-bromo-m-meconine (IX)

A solution of bromine (1.6 cc.) in glacial acetic acid (7 cc.) was added to glacial acetic acid (6 cc.), and 6-acetamino-*m*-meconine (3.4 gm. of m.p. 229.4–230.8°C.); the mixture was shaken thoroughly and allowed to stand for five hours. The resulting solution was diluted with water, treated with enough sodium bisulphite to remove excess bromine and with enough sodium bicarbonate to remove the mineral acid, and then chilled. The crystals which deposited were recovered, thoroughly extracted with water, and twice recrystallized from dilute methanol. Glistening white needles were obtained in a yield of 3.25 gm. or 73%, m.p. 188.2–189.2°C. Calc. for $C_{12}H_{12}O_5NBr$: C, 43.64; H, 3.64%. Found: C, 43.16, 43.31; H, 3.82, 3.59%.

6-Amino-3-bromo-m-meconine

Pure 6-acetamino-3-bromo-*m*-meconine (2.77 gm.) was heated under reflux for one and one-half hours with dioxane (10 cc.) and concentrated hydrochloric acid (12 cc.). The mixture was then cooled, brought to neutrality, and chilled. Brown, somewhat tarry crystals deposited, and were recovered, washed with water, and recrystallized from dilute methanol with the help of charcoal. The light brown needles so obtained, m.p. 122.2–124.7°C. were then sublimed under a pressure of 0.1 mm. and again recrystallized from dilute methanol. Pure white needles of m.p. 125.2–126.0°C. were obtained in a yield of 0.98 gm. or 41%. Calc. for $C_{10}H_{10}O_4NBr$: C, 41.67; H, 3.47%. Found: C, 41.69, 41.58; H, 3.42, 3.51%.

Deamination of 6-Amino-3-bromo-m-meconine

Pure 6-amino-3-bromo-*m*-meconine (0.408 gm.) was heated with water (50 cc.) and concentrated hydrochloric acid (8.4 cc.), but it did not all dissolve. The suspension was cooled to 0°C., treated with a solution of sodium nitrite (0.124 gm.) in water (15 cc.) and mechanically stirred at a temperature of less than 0°C. for two and one-quarter hours. The clear yellow solution was filtered onto ice; the filtrate was treated with hypophosphorous acid (5.2 cc. of a 30–32% solution) and kept in an ice bath for two hours and then in the refrigerator for 39 hr. Bright yellow crystals separated from the solution and were recovered, washed with water, and recrystallized four times from methanol, charcoal being used in the last three crystallizations. Pure white needles were obtained whose melting point was 182.9–183.6°C. Calc. for $C_{10}H_{10}O_4Br$: C, 43.96; H: 3.30%. Found: C, 44.13; H, 3.44%. A mixed melting point of these crystals with the pure 3-bromo-*m*-meconine obtained by direct bromination of *m*-meconine showed no depression.

Oxidation of m-Meconine

m-Meconine (m.p. 151–156°C., 15.6 gm.), acetic anhydride (66 cc.), and glacial acetic acid (49 cc.) were warmed together on the steam bath, the mixture being protected from atmospheric moisture. Red lead oxide (Merck's reagent Pb_3O_4 , 70.5 gm.) was added in portions during the course of 25 min.,

and then the reaction mixture was heated on the steam bath for four hours. A portion of the solvent was removed by distillation *in vacuo* and the undistilled residue was diluted with water (304 cc.) and chilled. Crystals were deposited and recovered, thoroughly washed with water, and dried in the air; yield 14.2 gm. These crystals were boiled for a few minutes with a dilute solution of potassium carbonate in order to decompose the acetyl derivative of *m*-opianic acid (13), and then filtered hot, the negligible precipitate being discarded. Acidification of the filtrate gave crystals which after being recovered and washed were very thoroughly extracted with cold dilute sodium bicarbonate solution for 45 min. The insoluble crystals were *m*-meconine since after recrystallization from water they melted at 154.6–155.0°C. not depressed by admixture with pure *m*-meconine. The recovery of *m*-meconine was 8.1 gm., or 52%. When the sodium bicarbonate extracts of the recovered *m*-meconine were acidified, crystals were recovered in a yield of 1.8 gm., m.p. 170–176°C., and a further 1.0 gm. of crystals soluble in sodium bicarbonate solution was recovered from various aqueous extracts from the experiment. The crude *m*-opianic acid (2.8 gm. or 17%) was twice recrystallized from methanol, charcoal being used in the first recrystallization, and the well shaped white needles which resulted weighed 1.65 gm. Their melting point of 140.7–141.6°C. showed them to be the almost pure methyl pseudo-ester of *m*-opianic acid (6). Calc. for $C_{11}H_{12}O_6$: C, 58.93; H, 5.36%. Found: C, 58.68, 58.41; H, 5.21, 5.28%. The conversion of the acid to its pseudo-ester was surprisingly easy, but the fact should be noted that the analysis for carbon and hydrogen was not a good criterion of the extent of the conversion.

Reaction of Some Substituted m-Meconines with Alkali

m-Meconines and the pseudo-esters of *m*-opianic acids dissolve slowly in alkali while *m*-opianic acids themselves dissolve instantly even in the cold. On acidification of their alkaline solutions, the *m*-meconines are recovered unchanged, the pseudo-esters are converted to the free acid, and the *m*-opianic acids are either unchanged or undergo the Cannizzaro reaction. When these characteristic tests are used to distinguish between these three classes of compounds, alcohols cannot be used to purify the recovered materials, on account of the easy formation of pseudo-esters.

6-Methoxy-m-meconine (m.p. 134.5–136.5°C. 0.32 gm.) made in the previous investigation (10) was heated on the steam bath with a dilute aqueous solution of potassium hydroxide. The solid dissolved completely after about two minutes. Heating was continued for about four hours; the warm solution was then cautiously acidified and chilled. The recovered crystals after one recrystallization from water were slender, glistening needles of m.p. 136.5–137.5°C., yield 0.22 gm. A mixed melting point showed them to be identical with the original material.

Pure *3-bromo-m-meconine* (0.80 gm.) from the direct bromination of *m*-meconine was treated in the same way. Solution required 20 min., and, after

one recrystallization of the product from dilute acetic acid, pure starting material was recovered in a yield of 0.73 gm. and identified by its melting point and mixed melting point.

6-Bromo-m-meconine (m.p. 206.2–207.2°C., 0.41 gm.) (10) after being heated with caustic, acidified, and recrystallized from dilute acetic acid, gave needles of m.p. 206.7–207.0°C. in a yield of 0.35 gm., which a mixed melting point showed to be the original material. Nearly 25 min. was required to bring about the solution of the crystals in hot caustic.

5-Iodooveratric Acid (XIV)

5-Iodooveratric aldehyde (37 gm.) (15) was stirred with water and sodium bicarbonate at 80–90°C. A warm solution of potassium permanganate (30 gm.) in water was slowly added. When the oxidation was complete, the manganese dioxide was removed and well washed with water. On acidification of the filtrate, a white flocculent precipitate of 5-iodoveratric acid was obtained in a yield of 94%. After it had been recrystallized from benzene or from glacial acetic acid, the 5-iodoveratric acid melted at 182–183°C. Calc. for $C_9H_9O_4I$: I, 41.23%. Found, by the method of Stepanow: I, 41.58%.

2-Iodooveratric Acid (XIII)

Crude 2-iodoveratric aldehyde (22.0 gm.) (16) was mixed with stabilized acetone (150 cc.), water (25 cc.), and sodium bicarbonate (4 gm.). Finely powdered potassium permanganate (18 gm.) was slowly added to the warm mixture, and the oxidation was soon complete. The reaction mixture was diluted with water, heated, and filtered, and the precipitate was thoroughly washed with hot water. Excess permanganate was destroyed with sodium bisulphite, the solution was filtered again, and the filtrate acidified to yield 2-iodoveratric acid. After one recrystallization from dilute alcohol with charcoal, the crystals were obtained in a yield of 16.2 gm. or 70%, m.p. 202–203.5°C. One more recrystallization gave the pure acid of m.p. 205–206°C. which was depressed by about 5° by admixture with either 2-chloroveratric acid or 2-bromoveratric acid. Calc. for $C_9H_9O_4I$: I, 41.23%; equivalent weight, 308.1. Found: I, 41.91, 42.07%; equivalent weight, 306.6.

6-Bromo-m-meconine (I)

6-Bromo-m-meconine (m.p. 206.2–207.2°C., 0.341 gm.) from the previous investigation (10) was once recrystallized from methanol, and the colorless crystals so obtained were as usual rigorously dried. The melting point of the purified crystals was 206.2–206.8°C. Calc. for $C_{10}H_9O_4Br$: C, 43.96; H, 3.30%; molecular weight: 273. Found: C, 43.53, 43.67; H, 3.40, 3.77%; molecular weight (on another analytical sample by the Rast camphor method): 296.

Acknowledgments

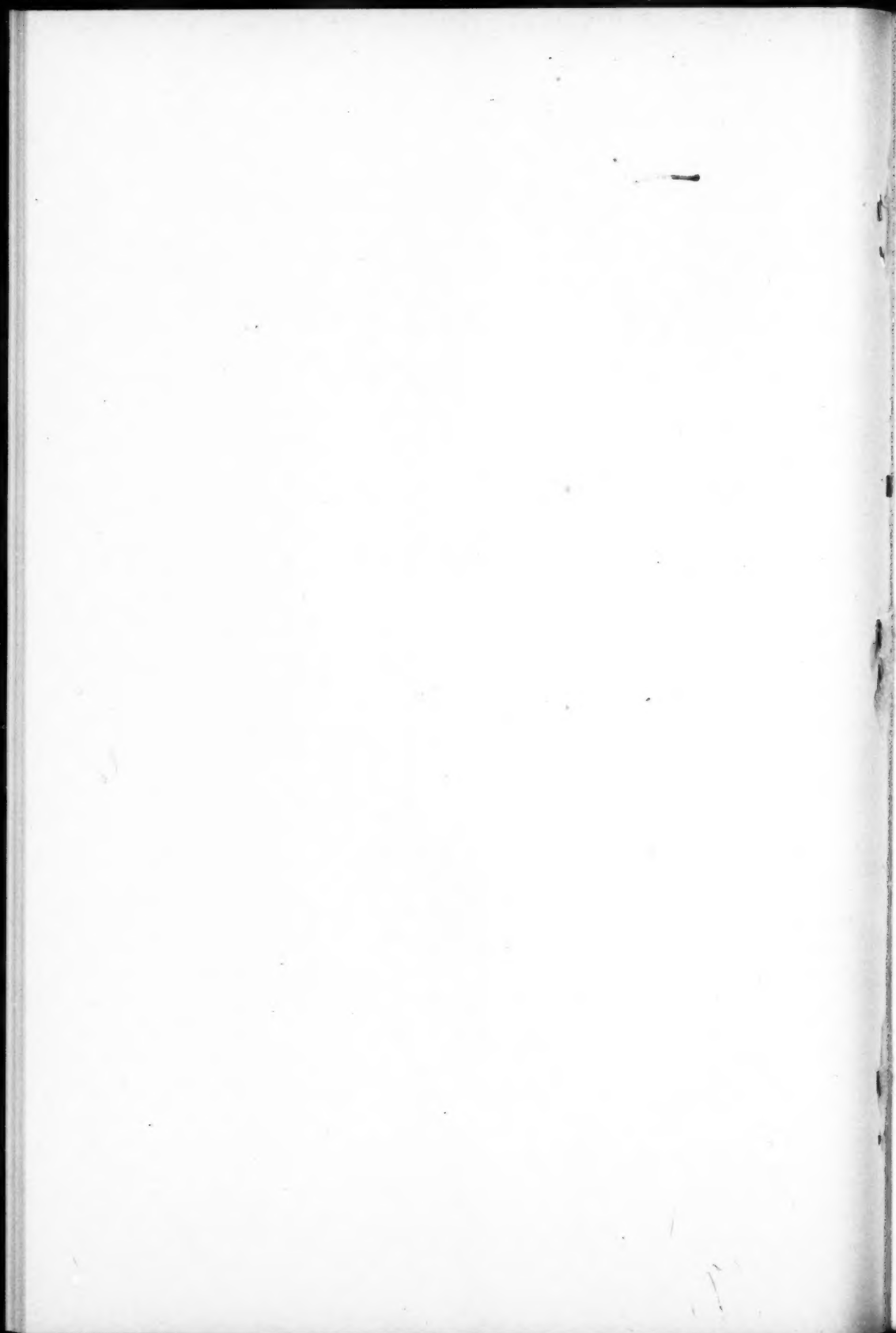
Microanalyses reported in the experimental section were performed by Mr. A. E. Ledingham and Mr. Ralph Mills of the Dominion Rubber Company.

The authors also wish to thank Mrs. Thelma Eskin Habgood, one of whose experiments on the reaction of 5-bromoveratric acid and formaldehyde is recorded in this paper, and Dr. Norah McGinnis (Mrs. W. Glen) for the preparation of 5-iodoveratric acid.

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